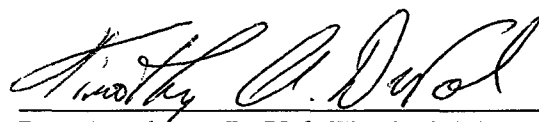


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To the Graduate School:

This thesis entitled "Uranium in Hot Water Tanks: A Source of TENORM" and written by Richard L. Woodruff Jr. is presented to the Graduate School of Clemson University. I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science with a major in Environmental Engineering and Science.

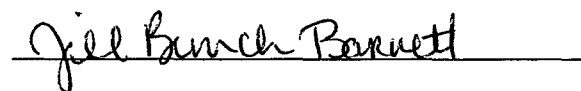

Dr. Timothy A. DeVol, Thesis Advisor

We have reviewed this thesis
and recommend its acceptance:


Dr. Robert A. Fjeld


Dr. David L. Freedman

Accepted for the Graduate School:



URANIUM IN HOT WATER TANKS: A SOURCE OF
TENORM

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Environmental Engineering and Science

by
Richard L. Woodruff Jr.

August 2002

Advisor: Dr. Timothy A. DeVol

DEDICATION

I dedicate this work to my loving wife, [REDACTED], and our three wonderful children, [REDACTED], and [REDACTED]. The fact that I could always look forward to coming home to you made the hours at work seem effortless.

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TABLE OF CONTENTS

	Page
TITLE PAGE	i
ABSTRACT	ii
DEDICATION	iii
ACKNOWLEDGEMENTS	iv
LIST OF TABLES	vii
LIST OF FIGURES	viii
 CHAPTER	
1 INTRODUCTION.....	1
2 BACKGROUND.....	5
Uranium Bearing Minerals	8
Aqueous Phase Geochemistry	10
Geochemical Computer Modeling.....	11
MINTEQA2	12
The Geochemist's Workbench, 3.0	12
Uranium Detection/Identification	13
Alpha Spectroscopy.....	13
Gamma-Ray Spectroscopy	14
Kinetic Phosphorimetry.....	15
X-Ray Fluorescence	16
Drinking Water Regulations	16
TENORM.....	17
Health Effects	18
Uranium via the Ingestion Pathway	19
Uranium in Specific Body Organs	20
3 OBJECTIVES	23
4 MATERIAL AND METHODS	24
Sampling Location Selection Process.....	24

Table of Contents (Continued)

	Page
Drinking Water Sampling Protocol	25
Hot Water Tank Measurements	27
Gamma-ray Imaging	29
XRF Analysis.....	30
Geochemical Computer Modeling.....	31
5 RESULTS AND DISCUSSION	33
Analytical Results	33
Drinking Water Analysis.....	33
Hot Water Tank Gamma Ray Spectroscopy	34
Corroboration of Analytical Results	39
Measurement of ^{238}U Short Lived Daughters	39
Gamma-ray Imaging	40
X-Ray Fluoroscopy	42
Geochemical Computer Modeling	44
6 SUMMARY AND CONCLUSIONS	50
APPENDICES.....	51
A Kinetic Phosphorescence Analyzer	52
B Alpha Spectroscopy For Location 2 Water	54
C Energy and Efficiency Calibration	58
D XRF Data.....	61
REFERENCES.....	63

LIST OF TABLES

Table	Page
Table 4.1 Drinking Water Parameters for Well Water at Residences in Simpsonville SC, Along With Average, Maximum, and Minimum Values for Well Water and Municipal Water Supplies *	26
Table 5.1 Drinking Water and Hot Water Tank Analysis Sample Locations*	34
Table 5.2 Estimated ^{235}U Activity From 144, 163, and 186 keV Peak Areas	37
Table 5.3 Hot Water Tank Activity, Specifically ^{238}U , ^{234}Th , and $^{234\text{m}}\text{Pa}$	40
Table 5.4 XRF Qualitative Analysis Results for Intensities of Elements Present Relative to Uranium (Intensity U/ Intensity Component)	43
Table C.1 ^{152}Eu Energy Calibration Data.....	59
Table D.1 XRF Qualitative Analysis Results for Intensities of Elements Present (Intensities in keps).....	62

LIST OF FIGURES

Figure	Page
Figure 1.1 DHEC Sampling for Uranium and Radium (Neel, 2002).....	2
Figure 2.1 Uranium Series (Shleien, 1992). All Energies in MeV. $E_{\gamma} < 0.05$ MeV Omitted, Gamma Intensity < 0.04 Omitted	6
Figure 2.2 Actinium Series (Shleien, 1992). All Energies in MeV. $E_{\gamma} < 0.05$ MeV Omitted, Gamma Intensity < 0.04 Omitted	7
Figure 2.3 Summary of Possible Paragenetic Relationships Among Several of the Most Important Uranium Mineral Groups that Occur in Oxidizing, Uranium Rich Systems (adapted from Garrels and Christ, 1959) (Jerden, 2001).	9
Figure 4.1 ORTEC PoPTop with Canberra Inspector 2000.....	27
Figure 5.1 Gamma-ray Spectrum From Hot Water Tank #2b (Live Counting Time = 2410 seconds).....	35
Figure 5.2 Graphical Representation of Uranium Precipitation Location Inside Hot Water Tank	41
Figure 5.3 The Geochemist's Work Bench Aqueous Speciation Prediction Using Input Parameters From Simpsonville Well Water (UO_2^{+2} concentration = 0.8 mg/L).	45
Figure 5.4 The Geochemist's Work Bench Precipitation Speciation Prediction Using Input Parameters From Simpsonville Well Water	46
Figure B.1 1000 $\mu\text{g/L}$ 10ml U Standard	54
Figure B.2 2000 $\mu\text{g/L}$ 10ml U Standard	55
Figure B.3 Location 2 Cold Water 10 ml Sample	56
Figure B.4 Location 2 Hot Water 10 ml Sample	57
Figure C.1 Efficiency Calibration Curve With Source 30cm From Detector	60

CHAPTER 1

INTRODUCTION

Elevated concentrations of uranium have been detected in private drinking water wells of residents near Simpsonville, South Carolina. Elevated levels of uranium were first detected by private sampling at one home in Simpsonville in January 2001. A member of the family living in the home had developed a benign brain tumor (WYFF, 2002). During the medical diagnosis, hair samples were analyzed in an effort to determine what might be the cause of the illness. Unexpectedly, elevated levels of uranium were found in the hair sample. This in turn led to an exploration of the cause. Drinking water samples were taken and analyzed by a local geologist, with results indicating a uranium concentration around 100 times greater than the United States Environmental Protection Agency's (EPA) maximum contaminant level (MCL). A second sample was performed with similar results, and the family notified the South Carolina Department of Health and Environmental Control (DHEC). Upon notification (February 2001), DHEC performed sampling at this location and at the houses on either side. DHEC results from all three of these samples showed uranium concentrations above the MCL. As a result, further sampling was performed at all of the homes within a 2-mile radius of the initial location (46 total) of which 6 were found to also exceed the MCL for uranium. Following these results, another phase of sampling was begun in which an additional 28 private wells were sampled. Five of these exceeded the uranium MCL. In addition to private well sampling, all of the public drinking water wells within a seven-mile radius of the initial home were sampled, none of which exceeded the MCL.

Since the initial phase of sampling, further sampling has been performed throughout the upstate of South Carolina. In July 2001 testing of an additional 300 private drinking water wells began and was completed. To date, seven hundred and seventy eight (778) private wells have been sampled in the upstate region of South Carolina, with 80 of them having uranium levels above the MCL of 30 $\mu\text{g/L}$. Uranium was detected as high as 10,100 $\mu\text{g/L}$, with several wells greater than 1000 $\mu\text{g/L}$. Additionally, 332 public drinking water wells (in the 10 Upstate South Carolina counties) have also been sampled, with 7 exceeding the MCL. Figure 1.1 is a map prepared by DHEC showing the extent of the uranium (and radium) investigation.

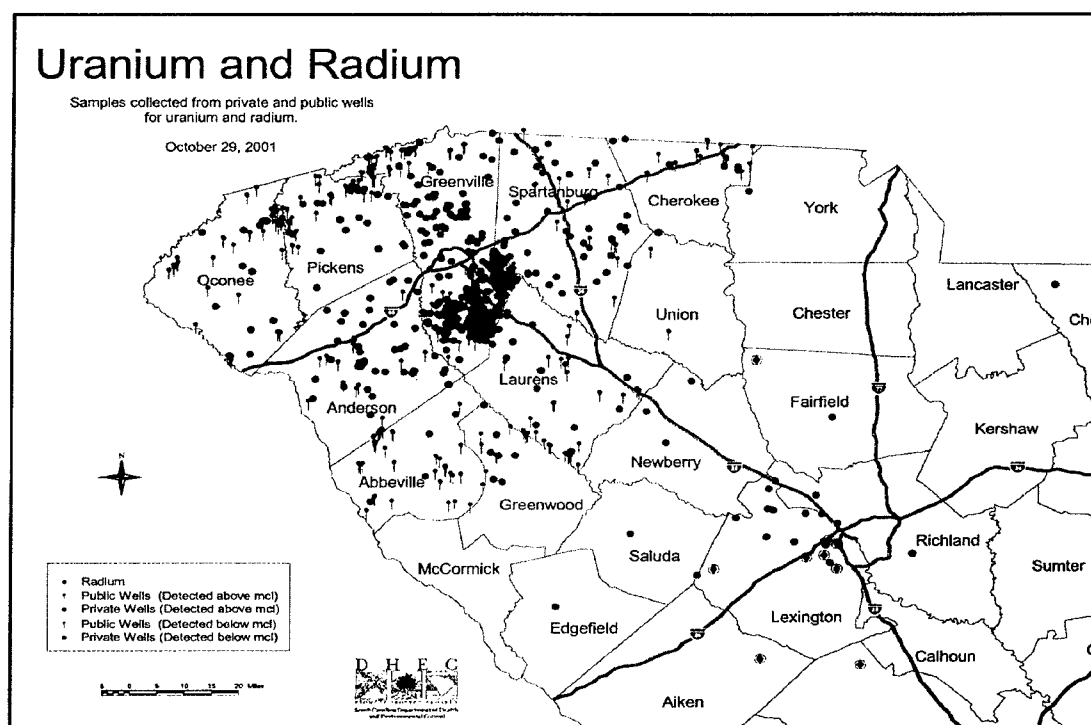


Figure 1.1 DHEC Sampling for Uranium and Radium (Neel, 2002)

In addition to the drinking water sampling, analysis has been performed on 105 residents (from homes with water results above the MCL) to determine uranium concentrations in urine. In March 2001 results from this sampling indicated that 94 of the 105 people had elevated levels of uranium in their urine (ATSDR, 2001). In February 2002 a second round of testing was performed on 79 of the original people. Of these, 63% had a decrease in the uranium concentration in their urine, while 37% showed an increase after about 12 months of not ingesting the uranium laden water (ATSDR, 2002).

Corrective action is diverse and varies depending on the location of the homes affected. Initially, a central source of drinking water was supplied to residents at no charge. Since then, municipal waterlines have been supplied to one large impacted neighborhood; however, cost prohibits this from being the practical solution for the entire Simpsonville/Fountain Inn area. Culligan of the Piedmont has donated an in-house treatment system to one home in an effort to see how their technology can be used for outlying areas. Additionally, other brands of home treatment units have been purchased by DHEC and residents, and installed with mixed levels of success at removing the uranium in the water (Neel, 2002). Some homeowners have decided to purchase water that is supplied directly to the home by a delivery service until long-term solutions can be reached.

Many questions and concerns have risen from this discovery and Clemson University's Department of Environmental Engineering and Science (CU EE&S) has worked with the local community to provide technical support and research assistance, to include sampling support for the ground water analysis, indoor radon analysis, and the effectiveness of local household treatment devices in removing uranium. The focus of

this research is to investigate how the hot water heaters could affect the uranium concentrations in the water and potentially concentrate the uranium inside the tank, creating TENORM.

CHAPTER 2

BACKGROUND

Uranium is a primordial radionuclide created during the formation of the earth. It has a 4.7 billion year half-life and is ubiquitous in the environment. Uranium can be found in rocks and soils including granite, metamorphic rocks, lignites, monazite sand, and phosphate deposits (Hess et al., 1985) with a typical concentration in materials of a few parts per billion (ATSDR, 1999). Natural uranium is a composite of three isotopes with long half-lives ($t_{1/2}$): ^{238}U (99.28% abundance, $t_{1/2} = 4.7 \times 10^9$ yr), ^{235}U (0.72% abundance, $t_{1/2} = 7.04 \times 10^8$ yr), and ^{234}U (0.0057% abundance, $t_{1/2} = 2.54 \times 10^5$ yr) (Firestone, 1996). Each of these isotopes emits alpha radiation with a significant emission fraction and produces a long decay series of progeny. Additionally, ^{235}U emits gamma radiation with high probability. Figures 2.1 and 2.2 depict the decay series for ^{238}U (Uranium Series) and ^{235}U (Actinium Series), respectively. Included are the modes of decay, half life of each radionuclide, the energy of the emitted radiation (in MeV) and intensities (%).

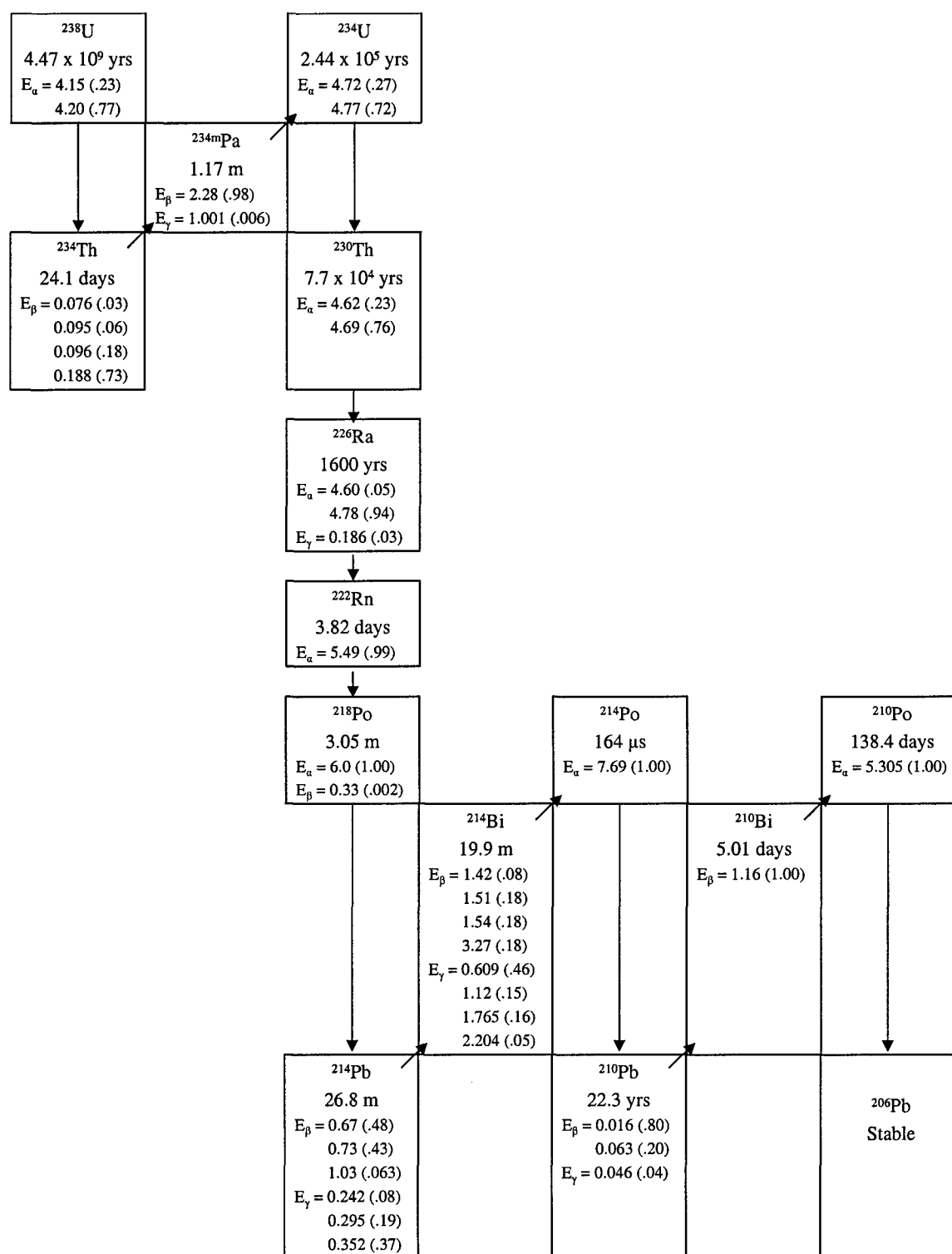


Figure 2.1 Uranium Series (Shleien, 1992). All Energies in MeV. $E_\gamma < 0.05$ MeV Omitted, Gamma Intensity < 0.04 Omitted

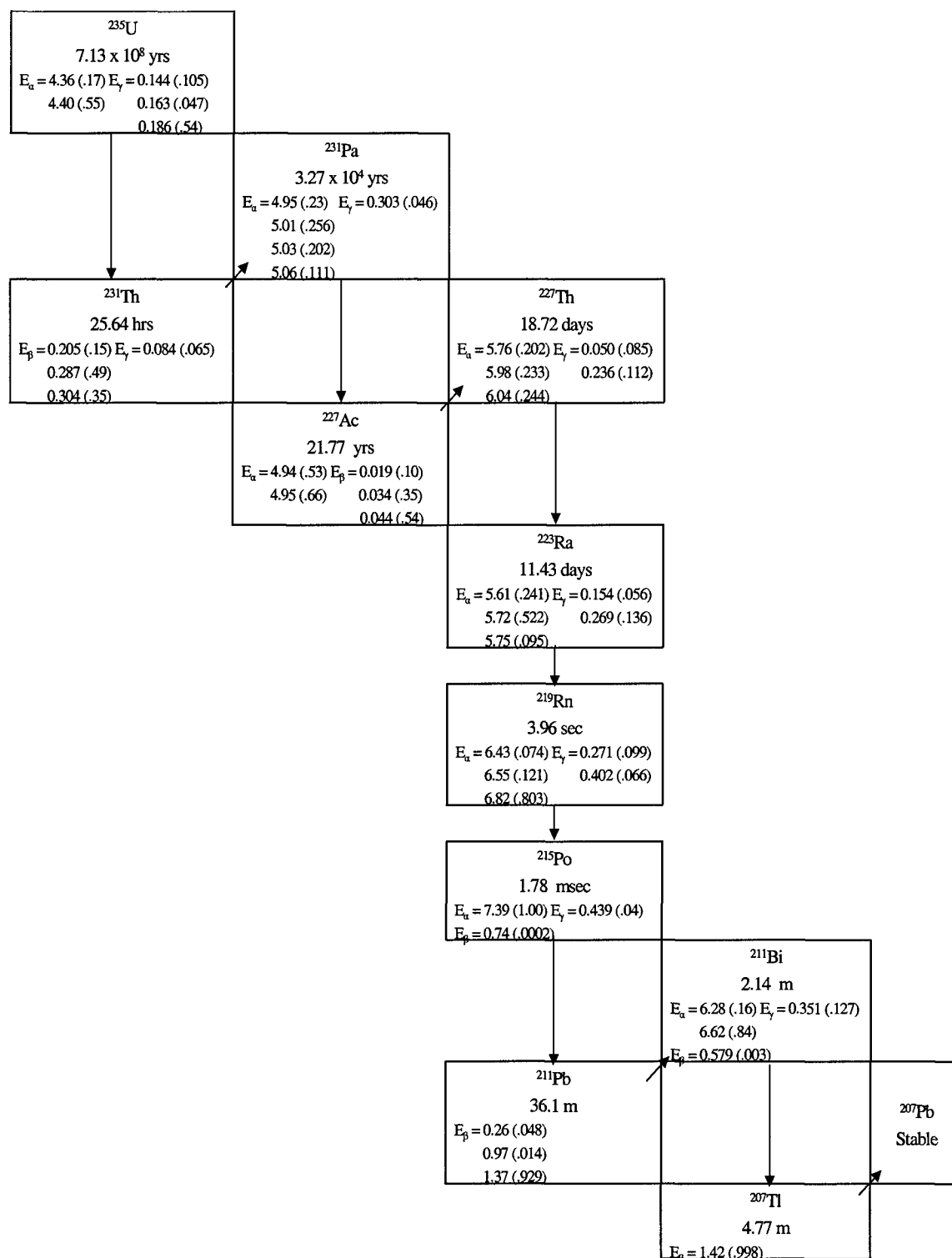


Figure 2.2 Actinium Series (Shleien, 1992). All Energies in MeV. E_γ < 0.05 MeV Omitted, Gamma Intensity < 0.04 Omitted

Uranium Bearing Minerals

Uranium is present as an essential structural constituent in nearly 5 percent of all of the known minerals, encompassing nearly 200 individual mineral species (Finch and Murakami, 1999; Burns, 1999). These minerals display a wide range of structural and chemical diversity, which results from the different chemical conditions under which the uranium minerals were formed (Finch and Murakami, 1999). As a result, according to Finch and Murakami (1999), uranium minerals provide an excellent indicator of the geochemical environment, which is closely related to the geochemical element cycle. The most complete descriptions of uranium minerals, according to Finch and Murakami, have been provided by Frondel (1958); however, with increasing knowledge of uranium mineralogy and crystal chemistry, many updates have occurred during the past 40 years. Smith (1984) has provided an additional review of more recent discoveries in uranium mineralogy, which includes structures, occurrences, and mineral descriptions for updated minerals (Finch and Murakami, 1999).

Uranium(IV) and uranium(VI) are the most common forms of uranium present in minerals. The uranium(IV) minerals are much less soluble than hexavalent uranium. Of the reduced (U^{4+}) uranium minerals, uraninite (U_3O_8) is the most important mineral in terms of abundance and economic value (Finch and Murakami, 1999). Uraninite is a simple oxide. Coffinite [$U(SiO_4)_{1-x}(OH)_{4x}$] and uranophane [$Ca(UO_2)_2Si_2O_7$], both hydrated uranium silicates, are also common uranium minerals. All of these minerals can be oxidized to the U^{6+} state, which allows them to become more soluble.

In addition to the reduced mineral species, there are numerous uranyl minerals. In aqueous environments, the U^{6+} always bonds strongly to two oxygen atoms, forming the

approximately linear uranyl ion, UO_2^{2+} (Finch and Murakami, 1999). The dissolved uranyl ion comes from the oxidative dissolution of the uranium-bearing minerals, with the mineral constituents playing a role in determining solubility. Figure 2.3 is a pictorial representation of the paragenesis of several uranyl-mineral groups.

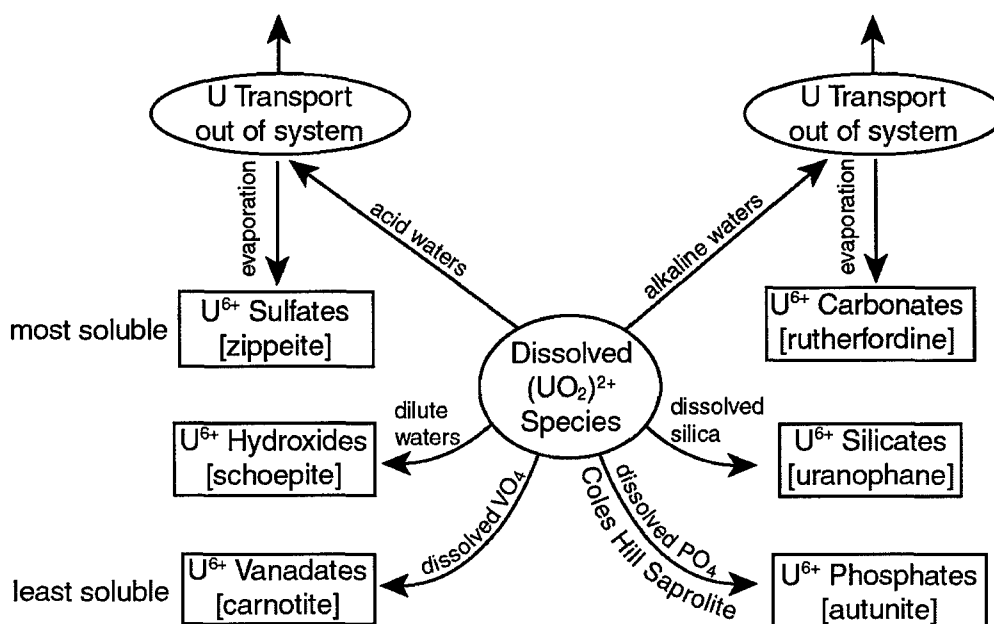


Figure 2.3 Summary of Possible Paragenetic Relationships Among Several of the Most Important Uranium Mineral Groups that Occur in Oxidizing, Uranium Rich Systems (adapted from Garrels and Christ, 1959) (Jerden, 2001).

The dissolution of the uranium from the mineral species is key to the mobility of the uranium in subsurface transport, and the resulting bioavailability. Finch and Murakami (1999) provide detailed descriptions of the alteration of reduced uranium minerals as well as alterations of uranyl-mineral, which effect the uranium concentrations in ground water.

Aqueous Phase Geochemistry

The presence of uranium in an aqueous phase is dependent on the solubility of the mineral as depicted in Figure 2.3, in addition to the valence state. As a result, the hexavalent state is most important for drinking water concerns (Cothorn and Lappenbusch, 1983) and is typically found as either di- or tri- carbonate anion (Hess et al., 1985), which are soluble over a wide range of conditions (De Vivo et al., 1984). According to Hayes et al. (2000), the National Council on Radiation Protection and Measurements Report 94 identifies numerous factors affecting the solubility of uranyl complexes. These include pH, temperature, redox potential (closely tied to the dissolved oxygen content), concentration of dissolved solids, and flow rate, which can be discounted when discussing ground water. In 25°C water, soluble uranyl fluorides are formed at a pH < 4, uranyl phosphates are formed at a pH 4 – 7.5, and uranyl di- and tri-carbonate complexes are formed at pH > 7.5 assuming those anions are present at sufficient concentrations (De Vivo et al., 1984).

With uranium ubiquitous in the environment, uranium is a common constituent in natural waters including seawater, freshwater, and surface and ground water (Hayes et al., 2000), thus, it is expected that some drinking water sources will contain concentrations of uranium (Cothorn and Lappenbusch, 1983). Uranium concentrations in ground water depends on factors such as, but not limited to, the uranium concentration in the host aquifer rock, the presence of oxygen and complexing agents, chemicals in the aquifer, chemical reactions with ions in solution and the nature of the contact between the uranium minerals and the water (Hess et al., 1985). According to Hess et al. (1985), these factors vary throughout the United States due to rainfall, geology and ground water

flow patterns, and to anthropogenic factors such as use rate of ground water and surface water, which allows for large variations of uranium concentrations from area to area.

Uranium levels in ground water vary across the United States. Typical U.S. concentrations of uranium in surface water are 1 – 10 µg/L and 1 – 120 µg/L for ground water. Ground water in uranium mines typically contains 15 – 400 µg/L, and the leachate from uranium mill tailings typically contains 10,000 – 20,000 µg U/L (Hess et al., 1985). According to the Agency for Toxic Substances and Disease Registry (ATSDR) (1999), most drinking water supplies in the U.S. contain natural uranium levels below 1.5 µg/L although elevated levels can occur. According to Hayes et al. (2000), a number of states have found average uranium drinking water levels exceeding 6 µg/L. In a survey of nearly 30,000 public surface and ground water supplies 7% contained uranium at or above 30 µg/L (Cothorn and Lappenbusch, 1983). The predominant uranium isotopes in naturally occurring water are ^{238}U and ^{234}U at natural activity ratio ($^{234}\text{U}/^{238}\text{U}$) typically between 1 and 3; however, values as high as 28 have been observed (Hayes et al., 2000).

Geochemical Computer Modeling

Modeling of closed environmental systems is commonly used to predict how chemicals will react under a given set of conditions. Computer models can be used to aid in the assessment and prediction of these reactions under equilibrium conditions and help corroborate experimental results. Two chemical equilibrium computer models are MINTEQA2 and The Geochemist's Work Bench Version 3.0. Both models are thermodynamic equilibrium models in which kinetics of the reactions are not taken into account. Because of this, the models produce similar results. Sutton (1998) compared previous MINTEQA2 modeling predictions with predictions from the Geochemist's

Work Bench, giving results in agreement with the previous work. The Geochemist's Work Bench provides the capability to produce equilibrium speciation diagrams (as well as other graphical representations) directly, whereas the MINTEQA2 results would have to be manipulated using another software program.

MINTEQA2

"MINTEQA2 is a geochemical equilibrium speciation model capable of computing equilibria among the dissolved, adsorbed, solid, and gas phases in an environmental setting" and is used to predict equilibrium speciation for dilute aqueous systems (U.S. EPA, 1991). The software contains an extensive database of thermodynamic data that is used in predicting the equilibrium situations. The data required for this model consist of a chemical analysis of the sample to be modeled with total dissolved concentrations for the components of interest and other relevant parameters (pH, temperature, etc.). The model can also be used to predict K_d , the distribution coefficient between adsorbed and dissolved concentrations. Since the EPA provides the software at no cost, it has been used extensively for modeling, including acid mine drainage (Johnson, 1993) and uranium interactions with mineral surfaces (Payne, 1999).

The Geochemist's Workbench, 3.0

"The Geochemist's Workbench is a set of software tools for manipulating chemical reactions, calculating stability diagrams and the equilibrium states of natural waters, tracing reaction processes, and plotting the results of these calculations" and uses several versions of a thermodynamic database (Bethke, 1998). Each database contains the properties of aqueous species, minerals, and gases, and equilibrium constants for

reactions to form these species, and data to calculate activity coefficients (Bethke, 1998) originally produced by the Lawrence Livermore National Laboratory. It has been used in applications such as modeling of the absorption of aluminum on quartz (Bickmore et al., 2001), removal of uranium and arsenic from ground water (Mallants et al., 2001), and uranium solubility in cement columns (Sutton, 1998).

Uranium Detection/Identification

Uranium detection can be accomplished by many different analytical and radiochemical methods. One way of detection is based on radiation emissions. As mentioned above, uranium emits different types of radiations. This fact is critical in the detection and identification of unknown radioactive material. Since uranium emits alpha and gamma radiation, different detection methods can be used depending on the material, situation, and context of the sampling.

Alpha Spectroscopy

Alpha particles are highly energetic doubly ionized helium nuclei that are emitted from the nucleus of the radioactive isotope and are essentially monoenergetic (Cember, 1996). As the particle travels, it continuously deposits energy throughout its path. The detection of this energy is essential in the quantification of the alpha particle; however, because of the continuous loss of energy, the range of alpha particles is only a few centimeters through air. For 5.0 MeV alpha particles, which are more energetic than those emitted by ^{234}U and ^{238}U , the mean range in air is about 5 cm. Comparatively, the range for a similar energy particle through aluminum is about 0.0024 cm (Cember, 1996).

Silicon diode detectors have become the detectors of choice for the majority of applications in which heavy charged particles (such as alpha particles) are involved

(Knoll, 2000). Alpha spectroscopy is a common application of the silicon diode detectors. Since alpha particles are monoenergetic, full-energy peaks are observed in the pulse height spectrum from the alpha spectroscopy system. The energy of the alpha particle is characteristic of the radionuclide from which it was emitted.

Gamma-Ray Spectroscopy

Gamma-ray photons are uncharged and create no direct ionization or excitation of the material through which they pass. "The detection of gamma rays is therefore critically dependent on the gamma ray undergoing an interaction that transfers all or part of the photon energy to an electron in the absorbing material" (Knoll 2000). As opposed to the continuous slowing down of heavy charged particles or electrons, these interactions represent sudden and major alterations of the photon properties. Since the detector is unable to actually "see" the gamma-ray, it is the electrons produced through gamma ray interactions that are actually detected. Three primary interaction mechanisms have significance in gamma-ray spectroscopy: photoelectric absorption, Compton scattering, and pair production. More information regarding these interactions can be found in *Radiation Detection and Measurement* by Knoll (2000).

Two types of detectors are commonly used for gamma ray spectroscopy, inorganic scintillators [typically NaI(Tl)] and high-purity germanium (HPGe) semiconductor detectors. The choice of detector in a given application most often revolves about a trade-off between detection efficiency and energy resolution. The absolute detection efficiency for sodium iodide scintillators is typically higher than germanium detectors due to their "availability in large sizes, which, together with the high density of the material, can result in very high interaction probabilities for gamma-

rays" (Knoll, 2000). However, the energy resolution for scintillators is poor, especially when compared to germanium detectors. Germanium detectors have a clear superiority with regard to energy resolution (Knoll, 2000). Although there are several gamma rays of interest for the detection of ^{235}U (Figure 2.2), the gamma rays come from about 0.72% of the total uranium mass present in a natural source. The presence of multiple gammas emitted in a close energy range makes it preferable to use a high purity germanium detector versus a scintillation detector, although the 186 keV can be resolved with NaI(Tl).

As shown in Figure 2.1, ^{226}Ra also emits a gamma-ray with an energy of 186.1 keV, which could interfere with the peak area for ^{235}U . According to Wolf (1999), this interference can be corrected by indirectly determining the contribution of ^{226}Ra by measuring the gamma-rays from ^{214}Pb and ^{214}Bi , when secular equilibrium exists between these three radionuclides. An alternative is to compare the ratio of peak area for the ^{235}U gamma ray peaks (144, 163, and 186 keV). If the 144 keV/186 keV and 163 keV/186 keV ratios are 1, then ^{226}Ra is probably not present in a high enough concentration to cause significant interference with the peak area of the 186 keV gamma-ray, and no correction would be necessary (Reilly et al., 1991).

Kinetic Phosphorimetry

One atomic technique that has been used to measure total uranium is called kinetic phosphorimetry. Kinetic phosphorimetry analysis (KPA) provides a fast, sensitive, and accurate method for the direct detection of uranium in aqueous solutions from parts per million to parts per trillion levels by using a pulsed LASER (light amplification by stimulated emission of radiation) to excite the sample and measuring

luminescence intensity to determine concentration (Brina and Miller, 1993). Brina and Miller have benchmarked their KPA technique to determine its accuracy and precision by analyzing samples using this technique compared to radiochemical analysis and fused-pellet fluorimetry. They have shown that the KPA method provides the highest accuracy and precision of the three methods.

X-Ray Fluorescence

X-ray fluorescence (XRF) is a process that uses external X-rays to interact with a sample through photoelectric absorption. From the subsequent de-excitation of the sample, characteristic X-rays are emitted, which are used to determine the elements of the sample (Knoll, 2000). According to Wolf (1999), XRF can provide both qualitative identification and quantitative determination of uranium. The sample can be either liquid or solid. Qualitative analysis can be performed with practically any matrix and sample composition. However, for quantitative determinations solid samples should be homogenized and pressed or fused into pellets, and the matrix effects require matching of standards to the unknown sample to obtain accurate results (Wolf, 1999). Many different research groups have used XRF in an effort to detect uranium in lake sediments (Phedorin et al., 2000), for in situ detection of uranium in natural systems for geologic timescale evaluations (McCall et al., 2001), and for actinide characterization (Havrilla, 1997).

Drinking Water Regulations

The EPA has established a goal (Maximum Contaminant Level Goal (MCLG)) of no uranium present in drinking water but recognizes that given current treatment technology and cost basis, this level is unrealistic. As a result, the EPA established a

MCL of 20 $\mu\text{g/L}$ in 1991. This was based on the calculation that if 150,000 people drank 20 $\mu\text{g U/L}$ for a lifetime, there is a chance that one of them might develop cancer as a result of the uranium in the drinking water. In 1994 the EPA considered changing the MCL to 80 $\mu\text{g/L}$ based on newer human intake and uptake values and the high cost of removing uranium from the drinking water supplies. In 1998 however, the EPA temporarily dropped the 1991 limit (ATSDR, 1999). On 7 December 2000, the EPA finalized regulations setting the regulatory standard for uranium in drinking water at 30 $\mu\text{g/L}$, effective 8 December 2003 (Federal Register, 7 Dec 2000).

TENORM

TENORM has been recognized by government agencies, industries, and regulatory authorities for more than 20 years and comprise an array of naturally occurring materials that, due to human activity, may present a radiation hazard to people and the environment. TENORM is defined by the EPA as material that "...contain radionuclides that are present naturally in rocks, soils, water, and minerals and that have become concentrated and/or exposed to the accessible environment as a result of human activities such as manufacturing, water treatment, or mining operations" (U.S. EPA, 2000). In January 1999 the Committee on Evaluation of EPA Guidelines for Exposure to Naturally Occurring Radioactive Materials, of the National Academy of Sciences (NAS) and National Academy of Engineering (NAE) completed an evaluation of the risks from TENORM that was sponsored by the EPA. According to the NAS report TENORM is defined as "any naturally occurring material not subject to regulation under the Atomic Energy Act whose radionuclide concentrations or potential for human exposure have been increased above levels encountered in the natural state by human activities" (NAS,

1999). Although no direct regulations currently exist to monitor TENORM, it is regulated indirectly by application of various current regulations and policies. The EPA has developed standards under several different environmental laws including the Clean Air Act (CAA), the Clean Water Act (CWA), the Safe Drinking Water Act (SDWA), and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). The NAS however noted in their report that “neither EPA, which has primary responsibility for setting federal radiation standards, nor any other federal agency with responsibility for regulating radiation exposures has developed standards applicable to all exposure situations that involve TENORM” (NAS, 1999). Instead, the NAS found that “federal regulation of TENORM is fragmentary, and many potentially important sources of public exposure to TENORM are not regulated by any federal agency” (NAS, 1999).

Health Effects

Naturally occurring uranium is classified as both a radiological and toxicological agent and is the only radionuclide for which chemical toxicity is the limiting factor (Wrenn et al., 1985). “Uranium has been rated as highly toxic based upon the following definition (Goldwater, 1957): ‘Toxicity is the ability of a chemical molecule or compound to produce injury once it reaches a susceptible site in or on the body’”(Hayes et al., 2000). Due to its low specific activity resulting from its long half-life, natural uranium presents a very low radiological risk and it is considered to be primarily a stable element with regard to its biological action (Wrenn et al., 1985).

According to Hayes et al. (2000), “perhaps the most important factor influencing the potential health impact of natural uranium is its solubility.” Solubility affects both

the availability and exposure pathways of uranium with the route of exposure determining the health impact, where soluble uranium follows the ingestion pathway predominantly and insoluble uranium typically following the inhalation pathway (Hayes et al., 2000). Soluble uranium typically follows the ingestion pathway where it enters the blood stream and moves throughout the body. Insoluble uranium (since not typically present in water) is usually inhaled and is primarily retained in the lung compartment (Stannard, 1988). Health effects due to ingestion will be discussed in more detail. Hayes et al. (2000) provide a brief overview of inhalation health effects while the ATSDR's Toxicological Profile for Uranium (ATSDR, 1999) provides an in-depth discussion on ingestion, inhalation, and dermal exposure health effects.

Uranium via the Ingestion Pathway

The following is taken from Hayes et al. (2000) and provides a succinct overview of the ingestion pathway for Uranium:

The absorption of uranium into a biological system is dependent on a number of factors such as nutritional state, intestinal content, age (Bosshard et al., 1992), and the level of intake (Wrenn et al., 1985). According to Wrenn et al. (1985), maximum absorption (based on percentage) occurs at lower levels of intake rather than at higher levels of intake.¹ Internally, ingested uranium faces three possible fates: rapid elimination, absorption with short-term retention, and adsorption with longer-term retention. The majority of the ingested quantity, approximately 95%, is cleared via renal excretion with a biological half-life of 2 to 6 days (Bosshard et al., 1992). Based on numerous studies

¹ According to Wrenn et al. (1985), some dependence of uranium absorption on intake is anticipated from chemical considerations. At very low levels of uranium intake, absorption should be maximal because of (a) the availability of natural complexing agents, e.g. citrate, to stabilize UO_2^{+2} against reduction and precipitation and facilitate absorption, and (b) the thermodynamically favorable (mass law) condition of a low uranium concentration. Exhaustion of complexing agents in the intestinal contents and formation of insoluble diuranates and phosphates in the neutral-to-alkaline intestinal contents would act to reduce uranium absorption at high intake levels.

involving both animal and human subjects, it is currently thought that roughly 2% of ingested soluble uranium is absorbed into the GI tract (ICRP 78, 1997) although it may be as low as 1% (Durbin, 1998).

Absorbed uranium is available to all tissues in the body via blood transport. The target tissues of uranium, in terms of potential biological damage, are bone and kidney. It is in these two organs that the two actions of uranium, radiological and toxicological, are observed.

Uranium in Specific Body Organs

Again, Hayes et al. (2000) have provided a good summary of the health effects and processes involved with the ingestion of uranium in both the skeletal system and kidneys of the human body. The excerpts below are from their report:

Bone

Due to long-term retention and half-life of uranium, the risk to bone is radiological (Bosshard et al., 1992). Uranium is initially deposited on bone surfaces, especially growing surfaces (Durbin, 1998). Under equilibrium conditions, as is the case with chronic exposures, uranium is widely distributed through the bone volume (Wrenn et al., 1987). This redistribution is the result of uranium being buried by the growth of new bone surface, which allows for slow diffusion through the bone surface, which allows for slow diffusion through the bone volume (Durbin, 1998). Although uranium is a known volume seeker, there is no evidence directly relating uranium to cancer induction in humans (Mayes and Rowland, 1985; Wrenn et al., 1985; Wrenn et al., 1987; Stannard, 1988; Bosshard et al., 1992; ATSDR, 1999).

ICRP 30 (1979) recommends the use of a two-compartment model based on calcium to describe uranium retention due to the similarity in skeletal kinetics thus allowing use of the general metabolic model for alkaline earth elements. In this model, 20% of the absorbed fraction is deposited in bone with a biological half-life of 20 days and 2.3% of the absorbed fraction was deposited in bone with a biological half-life of 5000 days. In a more recent publication (ICRP 69, 1995) "it is assumed that 15% of uranium leaving the

circulation deposits on bone surfaces" with a biological half-life of 5 days. Approximately half of the uranium leaving the bone surface is returned to plasma while the other half moves to the "exchangeable bone volume (EBV)" compartment, which has a biological half-life of 30 days. Roughly 75% of the uranium leaving the EBV compartment is returned to the bone surface while the remaining 25% is committed to the "non-exchangeable bone" compartment with a biological half-life of 5000 days (ICRP 69, 1995).

Kidney

The obvious result of having a 2% absorption fraction is that approximately 98% of ingested uranium is passed through the kidneys and eliminated from the body. Additionally, the kidneys continue to filter the amount remaining in the blood, thus effectively filtering nearly 100% of ingested uranium.

A two-compartment model, similar to the bone model, describes deposition and retention of uranium in the kidney (ICRP 30, 1979). In the ICRP 30 model, 12% of the absorbed uranium is deposited and retained with a 6-day half-life, and 0.00052% is deposited and retained with a 1500 day half-life. According to ICRP 69, 63% uranium in the bladder contents results directly from circulation while an additional 12% enters from temporary deposition in the renal tubules. The 12% temporarily residing in the renal tubules is cleared with a 7-day half-life. This model accounts for 0.5% deposition in "other kidney tissue" with a half-life of 5 years, or 1825 days.

The importance of deposition and retention of uranium in the kidney is based on potential impairment of kidney function. The nephrotoxic action of uranium is a complex process and will not be discussed in detail here as it has been described by numerous authors (Voegtlin and Hodge, 1949; Tannenbaum, 1951; Leggett, 1989; Bosshard et al., 1992; Durbin, 1998). In general, free UO^{2+} can preferentially occupy Ca^{2+} binding sites in the brush-border membrane of the proximal tube where it can be incorporated into brush-border cells during the membrane renewal process (Durbin, 1998). Primary renal damage results in chemical changes in the blood and urine while secondary changes occur in structure or function of other tissues (Durbin, 1998). Extensive structural changes have been observed in the brush-border membrane after high

dosages of uranium (Leggett, 1989). Damage to other portions of the kidneys may occur if the dosage is high enough, but, unless the damage is "severe," the kidneys normally recover completely (Stannard, 1988). Recovery from high doses of uranium has been found to result in the development of a tolerance to subsequent exposures (Leggett, 1989).

Chapter 3

OBJECTIVES

The objective for this thesis was to determine if uranium in ground water could concentrate inside the hot water tanks of homes in the Simpsonville community resulting in the hot water tank being classified as TENORM. The primary task of this objective involved the deployment of the CU EE&S portable HPGe system to take gamma-ray measurements of the hot water heaters of four homes and estimate the total amount of uranium present in the hot water tanks. The selection of the homes was based on results from well water sampling to ensure the presence of uranium entering the system. Corroborative efforts included sampling of the pre- and post-treatment water exiting the hot water tank and comparing uranium levels with the unheated water. These efforts also included: modeling the uranium speciation with MINTEQA2 and Geochemist's Workbench using the ground water characterization available to predict what form the uranium is in and if it precipitated in the hot water heater; corroborating the composition of the precipitate in the hot water tanks by XRF analysis; and using the models to predict uranium concentrations/fate of the uranium precipitate in the hot water tanks once the community converts over to the municipal water system.

Chapter 4

MATERIAL AND METHODS

Sampling Location Selection Process

DHEC has sampled over 750 private and public drinking water wells in the Simpsonville area, with uranium levels ranging from non-detected to 10,100 µg/L. A summary of these results was provided to CU EE&S and was used in selecting homes with elevated levels of uranium (above the MCL). Since one underlying objective is to determine if uranium would concentrate in the hot water tank, homes with elevated levels of uranium in their water supply were desired. Although numerous homes fit this requirement, four homes with five hot water tanks were selected for this study. Homeowner cooperation was key in this selection process, especially since the sampling of the drinking water and hot water tanks required access to the home. Additionally, it was desired to have a home where the corrective action (treatment system or municipal water supply) would occur during the duration of this work.

All four of the residences had elevated levels of uranium, exceeding the MCL by 10 to more than 200 times. Location 1 did not have any special treatment remedies during the duration of this project. This location was selected because it was the highest uranium in well water detected during the DHEC study (10,100 µg/L). Location 2 had an in-house treatment system donated by Culligan of the Piedmont. The final two homes, locations 3 and 4, were connected to the municipal water supply during the duration of this project. At each of the locations well water samples were collected and analyzed for uranium by KPA. Hot water samples were collected and, where applicable, post

treatment samples were collected both for hot and cold water. Also, the hot water tanks at the homes were analyzed by gamma-ray spectroscopy for uranium at all four locations. In addition, one of the hot water tanks donated to CU EE&S was used for extensive investigation. The extensive investigation included gamma-ray imaging the tank and XRF analysis of the sediment from the tank.

Drinking Water Sampling Protocol

Drinking water samples were collected from each well, as close to the wellhead as practical ensuring no treatment had taken place and hot water samples were collected from the kitchen sink, and were analyzed for total uranium. The uranium in water analysis was conducted with 10 – 100 μ L aliquant of a homogenized sample and analyzed with a ChemChek KPA system (serial number 90-05050045, model KPA-10, manufactured on May 1990) following manufacture procedures; Appendix A. The purpose of these samples was to corroborate the results of previous DHEC samples and to provide a baseline to compare with post-treatment cold and hot water samples. Cold and hot water samples were taken from the kitchen sink, except at location 1, where inside access was unavailable. For this location, a sample was collected directly from the drain port on the hot water tank.

DHEC performed sampling for water quality parameters at multiple locations in the area, to include the four homes that are the focus of this research. Mr. Peter Stone from DHEC provided the results to CU EE&S. The results of the analyses from 25 residences in the Simpsonville area are summarized in Table 4.1.

Table 4.1 Drinking Water Parameters for Well Water at Residences in Simpsonville SC, Along With Average, Maximum, and Minimum Values for Well Water and Municipal Water Supplies

Variable 1	Alk ²	As	Ca	Cl	F	Fe	Mg	pH (SU)	K	Silica in Water	Na	SC ³	Sr	SO ₄ ²⁻ 4	TDS 5	U	D.O. 6
Location																	
1	50	ND	17	3.1	1.1	0.1	1.1	7.3	1.4	32	7.5	126	0.02	7.4	110	2.7	6.66
2	46	0.0077	15	2.7	1.1	ND	1.3	7.5	2.5	41	9.9	128	0.06	11	120	1.3	2.96
3	96	0.0054	36	3.9	1.1	ND	1.7	8.1	1.8	22	14	250	0.06	28	170	2.3	1.55
4	78	ND	38	3	1.6	ND	0.8	8.1	1.4	26	24	286	0.02	64	190	0.6	0.11
W Avg ⁷	35.8	0.0067	14	3.8	0.7	0.04	0.9	6.9	1.8	27	10	126.4	0.05	15.8	101	0.7	5.6
W Max ⁸	96	0.038	44	17	2.8	0.11	1.7	8.2	3.3	43	49	295	0.07	77	200	4.9	8.95
W Min ⁹	4.1	ND	0.2	1.8	0.1	ND	ND	5.9	1.0	8.6	4.5	28.4	0.01	5	32	ND	0.15
M ¹⁰ Avg	8.0	ND	2	6.0	0.9	ND	ND	7.6	0.8	9	7.7	NA	ND	ND	38	ND	NA
M ¹¹ Max	20	ND	7	7.2	1.2	ND	ND	10.4	1.2	12	11	NA	ND	ND	54	ND	NA
M ¹² Min	5.0	ND	0.8	3.0	0.3	ND	ND	6.5	ND	2.5	4.9	NA	ND	ND	20	ND	NA

¹All units as mg/L unless otherwise indicated ²Alkalinity measured as CaCO₃ ³SC = Specific Conductivity (μMOHs) ⁴Sulfate measured as Automated Colorimetric ⁵TDS = Total Dissolved Solids ⁶D.O. = Dissolved Oxygen ^{7,8,9}Average, maximum, and minimum concentrations for the entire well water sampling population (N=25).

^{10,11,12} Average, maximum, and minimum concentrations for Greenville Water System drinking water.
* Additional items were sampled for and found to be non-detected (ND) or not available (NA). These parameters include: Aluminum, Antimony, Barium, Beryllium, Boron, Cadmium, Chromium, Cobalt, Copper, Lead, Mercury, Manganese, Molybdenum, Nickel, Selenium, Silver, Tin, and Zinc.

Hot Water Tank Measurements

Gamma-ray spectroscopic field measurements were taken at five hot water heaters (one home has two hot water tanks in series) using a transportable HPGe detector (ORTEC PoPTop, model 6MX-2519-P-A, serial number 41-TN31514A) in conjunction with a Canberra Inspector 2000 (model IN2K, serial number 05010129) as shown below.

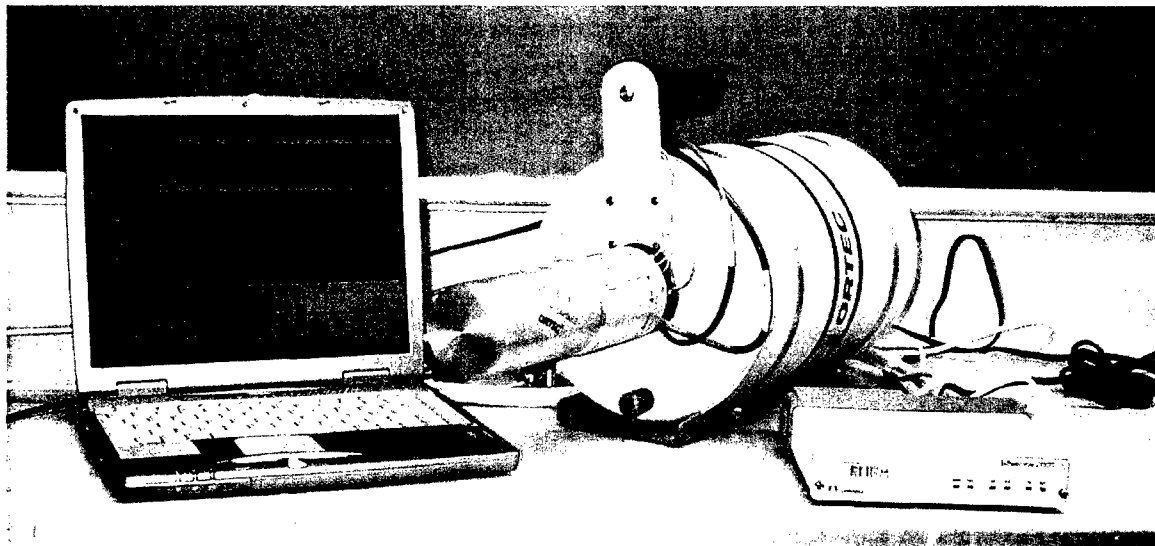


Figure 4.1 ORTEC PoPTop with Canberra Inspector 2000.

The purpose of the spectroscopy was to determine if uranium precipitates, and if so, estimate the amount of uranium that had accumulated in the hot water tank. In order to determine activity inside the tank, the absolute detection efficiency was estimated for the detector/geometry set-up. A 20-gallon plastic barrel was filled with well water, containing 7,667 $\mu\text{g/L}$ uranium, from location 1. The barrel was similar in diameter to

the hot water tanks but had a smaller volume. The detector was placed six inches from the bottom of the barrel, with lead bricks added below the detector to provide shielding from the ground. The tip of the detector was flush with the barrel. Since the activity of the water was known, back calculations using total counts within the 185.7 keV region of interest (ROI) for ^{235}U could be performed to estimate the absolute efficiency for a homogeneous source. Note: this well did not contain measurable ^{226}Ra . This homogeneous source efficiency calculation is a rough estimate for the hot water tank geometry where it is known that a heterogeneous source distribution occurs.

The mass of uranium in each of the hot water tanks was estimated based on the measured absolute detection efficiency (ϵ). Measurement of the hot water tanks was performed in a manner similar to that described above for the absolute detection efficiency calculation with the exception that the detector was located within 12 inches of the heating element panel for all tanks. Uranium mass (M_{uranium}) estimation was performed by using the following equations:

$$A_{^{235}\text{U}} (\text{Bq}) = \frac{\text{ROI}_{^{235}\text{U}} (\text{cps}) - \text{ROI}_{\text{background}} (\text{cps})}{\epsilon f} \quad (1)$$

$$M_{^{235}\text{U}} (\text{g}) = A_{^{235}\text{U}} (\text{Bq}) \times 1.2487 \times 10^{-5} \frac{\text{g } ^{235}\text{U}}{\text{Bq } ^{235}\text{U}} \quad (2)$$

$$M_{\text{uranium}} (\text{g}) = \frac{M_{^{235}\text{U}} (\text{g})}{0.007204} \quad (3)$$

The activity (A) in bequerels (Bq) was obtained by the net count rate (net cps) for the 186 keV gamma-ray ROI, ϵ , and the emission fraction (f) for the specific gamma-ray (in this case, $f = 0.54$). The live count time was 2410 seconds from both the tank and the background. This calculation provides the estimated activity due solely to ^{235}U . The activity from ^{235}U could also be obtained by the same procedure just described using the peak area for one of the other gamma rays emitted, shown in Figure 2.2. The mass of ^{235}U can be estimated based on the measured ^{235}U activity and the specific activity, equation 2. Since natural uranium is only 0.7204% ^{235}U by weight, the total uranium mass can be estimated by dividing the mass of ^{235}U by 0.007204. The total mass of uranium inside the tank is based on the total amount of uranium in the tank at the time of the measurement. In actuality, the uranium in the liquid phase represents a small fraction of the total uranium being detected inside the tank.

All hot water tanks were analyzed in place while operational at the residence. The first location had the heater located in a closet accessible from the outside of the home (a mobile home), at floor level with the living area, approximately 4 feet above the ground. The second and fourth homes had their hot water tanks located in the crawl space under the house, while the third location had the tank located upstairs in a closet. Background readings were taken in the same general setting (i.e. in the crawl space or upstairs) as the tank location, with the detector pointed away from the tank and located at least 3 feet from the tank itself.

Gamma-ray Imaging

One hot water tank was used to perform a gamma-ray imaging study in an effort to help predict where the majority of the uranium settled/accumulated in the tank. It is an

electric tank manufactured by A.O. Smith Water Products Co. (model ELJF 50, serial number MJ87-0074866-H43) that is 32 inches tall and has a diameter of 25.25 inches and contains two heating elements, located 7.5 and 18 inches from the bottom. The HPGe detector mentioned above was also used for this study.

The hot water tank was imaged using a collimated detector geometry. The tank was collimated into 5 horizontal levels, each being 6.44 inches in height. It was also sectioned off into vertical quarters identified as hands of a clock. Looking down onto the tank from the top, the heating elements were the 6 o'clock position, with the 9, 12, and 3 o'clock positions also identified. Gamma-ray spectroscopic analysis was performed at each level and each position, for 3600 seconds. The collimated detector was set up by placing the end cup of the HPGe detector 8 inches from the outside of the tank, with lead bricks (4"x2"x8") placed above and below the detector and the 8 inch gap between the end cup and the outside of the tank. Wood slats were used to support the top layer of bricks. This geometry and shielding allows the imaging of a vertical section 6.44 inches tall at the center of the tank. Side collimation was not utilized for this study. A background reading was also taken in the laboratory with the tank removed from the room and used to obtain net background counts.

XRF Analysis

XRF analysis was performed on samples obtained from hot water tanks #1 and #4. XRF analysis was performed on sediment that flowed freely from the bottom of tank #4 and scale obtained from each of the heating elements of tanks #1 and #4. The XRF used for this analysis was the Rigaku X-Ray Spectrometer, model RIX 3000 (serial number: SR21029, data 1996). The spectrometer uses a NaI scintillation detector for the

detection of characteristic X-rays from heavy elements (elements heavier than manganese on the periodic table) and then uses a gas proportional counter for the detection of the characteristic X-rays for light elements (those lighter than iron). The range for heavy and light does overlap some. The samples were run using a helium atmosphere, which helps reduce interference/absorption of the X-rays. The sample protocol was to first run a heavy element scan, followed by individual scans looking for lighter elements. Specifically, the light elements scanned for were calcium, potassium, chlorine, sodium, phosphorous, silicon, aluminum, magnesium, fluorine, oxygen, nitrogen, carbon, and manganese. Other light elements were left out because they were not expected to be present based on well water quality parameters. The heavy element scan is not specific to individual elements; rather the entire spectrum is accumulated and then peaks are identified based on the characteristic X-rays produced from the heavier elements.

The samples were prepared by placing the material in an X-Cell container (3565 43mm X-Cell produced by Spex CertiPrep). Mylar (3516 Mylar, 0.12 mil thick, produced by Spex CertiPrep) was used to cover the top so the material would not spill inside the machine. The samples were not ground or pulverized in any fashion, nor pressed or made into pellets. As a result, the analyses are qualitative. A background sample was also analyzed using an empty X-Cell covered with Mylar.

Geochemical Computer Modeling

MINTEQA2 and The Geochemist's Work Bench, version 3.0 were used to model the environmental system that occurred in the subsurface as well as that in the hot water tanks. The objective was to use the models to predict/corroborate the results seen from the sampling and XRF analysis. Two conceptual model conditions were used. First, both

models were run using input parameters representative of the local well water in the Simpsonville area at both ambient (ground water) temperature and at an elevated temperature (representative of the hot water tank). This was done to predict what would happen if well water containing uranium were to enter an environment (the hot water tank) where the temperature was elevated. This modeling condition was run for varying pH, Eh, and temperature conditions, using the average, maximum and minimum water quality parameters shown in Table 4.1. In addition, the model was run using water quality parameters from location 4 because XRF analysis was performed on sediment from this hot water tank. Following this, both computer models were again run using the water quality parameters obtained from the Greenville Water System, Table 4.1. These water quality parameters are representative of the municipal water that is now connected to many of the homes in the area and two of the homes in this study. In this modeling, a solid amount of uranium mineral was assumed present in the hot water tank, and the computer models were used to predict if the solid would dissolve into the Greenville Water System water.

Chapter 5

RESULTS AND DISCUSSION

Analytical Results

Drinking Water Analysis

Uranium in drinking water analyses were performed by CU EE&S of the well water from four homes in Simpsonville. The measured values from these individual samples are shown in Table 5.1. In addition to the cold well water results, hot water samples were analyzed at locations 1, 2, and 4. There is a lower uranium concentration in the hot water relative to the cold water by 15% to 32.5%. In these samples, the only difference between the cold-water sample and the hot water sample is the presence of the hot water tank. No other treatment devices were present. In addition to these results, work performed by Ayaz et al. (2001) has shown that boiling the Simpsonville well water for 10 minutes causes a decrease in the aqueous concentration of uranium by about 16%. As a result, it was inferred that uranium was precipitating and settling in the hot water tank.

Post treatment samples were taken of both the cold and hot water at 3 homes. These results are also shown in Table 5.1. The term "post treatment" is used to generically describe all methods of treatment used in these four homes and can refer to a municipal water supply as well as water treated by units inside the home. Note: the hot water tank is not considered a treatment unit as referenced here. In the three locations where samples were obtainable, there was an increase in the uranium concentration for the hot water as compared to the post treatment cold water entering the hot water tank. In

all three cases, there was at least an order of magnitude increase in uranium concentration, with the largest being approximately 2.5 orders of magnitude greater. As seen in Table 5.1, all of the post treatment cold-water samples measured well below 30 $\mu\text{g/L}$. Of the three post treatment hot water samples collected, two were above the EPA's MCL (30 $\mu\text{g/L}$). These results also confirm the presence of uranium in the hot water tank and suggest the dissolution of the precipitated uranium into the post-treatment water.

Table 5.1 Drinking Water and Hot Water Tank Analysis Sample Locations *

Location Identification Number	Pre-treatment Water ($\mu\text{g/L}$)			Post-treatment Water ($\mu\text{g/L}$) ^a			Est. U in Hot Water Tank (g)	
	Cold	Hot	% removal	Cold	Hot	% increase		
1	7,667	6,491 ^b	15	na	na	na	3.5	
2	1,754	1,183 ^c	33	7.2 ^d	170	2,260	12 ^e	69 ^f
3	1,900	na	na	0.4 ^g	25.2	6,250	4 – 5	
4	732	568	22	0.4 ^g	60	15,000	29	

^a Hot water tanks still in use.

^b Sample taken directly from hot water tank drain port. Suspended solids had to be filtered.

^c Value based on % removal from alpha spectroscopy data available in Appendix B.

^d Culligan treatment unit consisting of aeration, ion exchange, carbon filter, and UV used for point of entry treatment.

^e Hot Water tank a (referred to as tank 2a).

^f Hot Water tank b (referred to as tank 2b).

^g Greenville Water System water.

* Except for hot pre-treatment water from location 2, all analyses were conducted with KPA.

Hot Water Tank Gamma Ray Spectroscopy

With analytical evidence supporting uranium precipitation in the hot water tank, gamma ray spectroscopy was deployed in the field to estimate/quantify the amount of uranium present in the tanks. Using the 20 gallon barrel filled with 7,667 $\mu\text{g/L}$ uranium

in water to approximate the 30 gallon hot water tanks, the absolute efficiency was calculated to be 0.04% based on the 186 keV gamma-ray of ^{235}U . Following this estimation of the absolute detection efficiency five hot water tanks were surveyed. The spectrum obtained of hot water tank #2b is presented in Figure 5.1. Present in the spectrum is the 186 keV peak area from ^{235}U , along with the 144 and 163 peaks. Additionally, the 63 and 93 keV peak areas from ^{234}Th gamma rays are present. Each of these peak areas are highlighted in red, with the background spectrum overlaid in green. Figure 2.1 also indicates the emission of a gamma ray at 53 keV from ^{234}U . The emission fraction for this gamma ray is only 0.12%. This peak was not seen above background in any of the spectra obtained from the hot water tanks, and therefore could not be used in an effort to compare ^{235}U information or total uranium mass inside the tanks. Based on the calculation presented in Chapter 4, the estimated total uranium present in each tank is provided in Table 5.1.

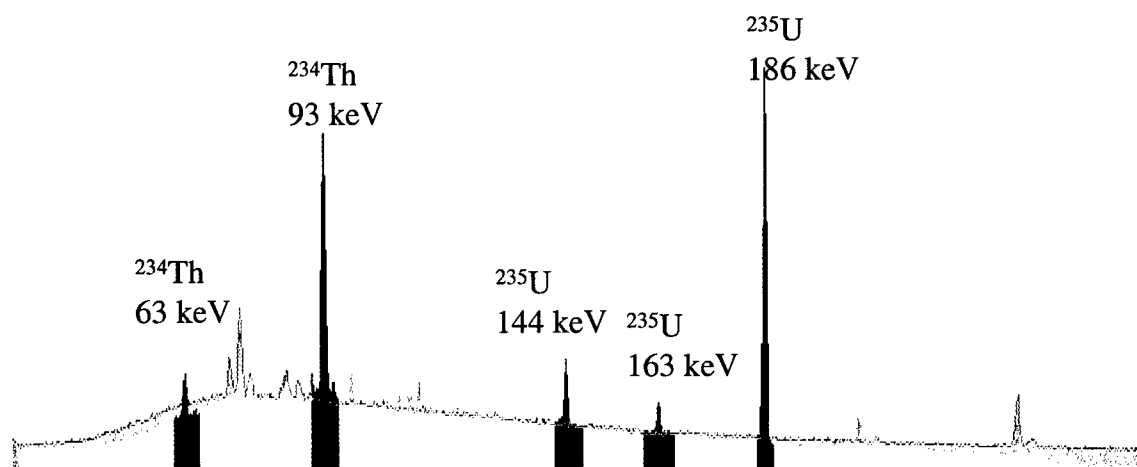


Figure 5.1 Gamma-ray Spectrum From Hot Water Tank #2b (Live Counting Time = 2410 seconds)

The 144 and 163 peaks were also noticeable in all spectra with the exception of tank 3. In an effort to quantify the ^{235}U activity separate from ^{226}Ra that may also be present inside the tanks, calculations were also performed using the peak area for the 144 and 163 keV peaks. The detection efficiency for these two peaks are slightly different from the 186 keV efficiency, however, the difference was neglected since the energies are relatively close; therefore, the same efficiency was used for all three energies when doing activity calculations. Table 5.2 provides these activities and activity ratios calculated based on the different energies and the propagated counting uncertainty. As discussed in the Gamma Ray Spectroscopy section of Chapter 2, if radium is present in the tank, there may be interference with the ^{226}Ra gamma ray (186.1 keV) and a correction would be necessary for the ^{235}U activity when using the 186 keV peak area. Using these ratios (144/186 and 163/186), it was not likely that there was significant interference from ^{226}Ra . Four of the five ratios are within statistical uncertainty of 1, indicating that the activity calculated from either the 144 or 163 keV peak areas is very close to the activity calculated using the 186 keV peak area. This in turn implies that the contribution of ^{226}Ra to the total peak area for the 186 keV gamma-ray is not significant, and further corrections are unnecessary. At location 4, this ratio is below 1, indicating that the activity as calculated from the 186 keV peak area is greater than that from the 144 and 163 keV peak areas, which might be due to the presence of radium, but additional analyses were not conducted.

Table 5.2 Estimated ^{235}U Activity From 144, 163, and 186 keV Peak Areas

Location Identification number	Activity (Bq) from			Ratio of activity for	
	144 keV	163 keV	186 keV	144 keV/186 keV	163 keV/186 keV
1	3389 \pm 177	4537 \pm 306	3329 \pm 83	1.02 \pm 0.059	1.36 \pm 0.073
2 a	7507 \pm 342	6663 \pm 371	7149 \pm 158	1.05 \pm 0.053	0.93 \pm 0.056
2 b	39,712 \pm 644	41,853 \pm 929	39,706 \pm 289	1.00 \pm 0.018	1.05 \pm 0.025
3	2188 \pm 142	Not seen	2382 \pm 80	0.92 \pm 0.067	NA
4	13,998 \pm 363	14501 \pm 545	16,858 \pm 190	0.83 \pm 0.023	0.86 \pm 0.034

Note: the peak area for the 163 keV peak at location 3 was not present above background
Uncertainty is reported here as the 1 - σ counting uncertainty.

Usage rate, temperature, and kinetics likely affect the accumulation of uranium in the tank. Usage can play an important role in the total uranium accumulated inside the tank as can be seen from the following "back of the envelope" calculation:

$$4 \frac{\text{people}}{\text{house}} \times 5 \frac{\text{minutes}}{\text{shower}} \times 8 \frac{\text{liters}}{\text{minute}} \times 1 \frac{\text{shower}}{\text{day person}} \times 365 \frac{\text{days}}{\text{yr}} = 58,400 \frac{\text{liters}}{\text{year}} \quad (4)$$

$$58,400 \frac{\text{liters}}{\text{year}} \times 1000 \frac{\mu\text{g uranium}}{\text{liter}} \times 0.2 \text{removal} = 12 \frac{\text{g uranium deposited}}{\text{year}} \quad (5)$$

For this sample calculation, 12 g of uranium is accumulated in the hot water distribution system of the home per year. The potential reservoirs for uranium accumulation other than the hot water tanks include the hot water pipes which were not included in this investigation. An additional consideration is that there is more usage of hot water than just showers. Usage is a direct multiplier in this accumulation, and as flow increases or decreases, it is expected the level of uranium accumulating inside the hot water tank will do the same. For example, location 1 is a mobile home that has typically had only one occupant over the past few years. Location 2 on the other hand is a family of 4 or 5, and it is expected the usage rate of hot water in this home is much greater than location 1. The hot water tanks were installed at least 5 years ago.

Of the five tanks, tank 2b had the highest estimated concentration at 69 grams of uranium. Tanks 2a and 2b are in series at this location that can conceptually be viewed as two continuously stirred batch reactors in series, resulting in the temperature conditions in tank 2b to be more constant than tank 2a (and the other tanks). The reasoning behind

this is the water entering tank 2b has already been heated by tank 2a, so less temperature variation takes place as opposed to ground water (cold) entering the tank and having to be heated, as is the case with tank 2a, and all of the other tanks in the study. Additionally, the kinetics for the formation of these minerals is likely to be very important. The water present in tank 2b has been held at the elevated temperature on average twice as long as in tank 2a. These observations are consistent with the greatest % removal being at location 2. This would help explain why other tanks that have higher concentrations of uranium entering in the well water have less uranium accumulated inside the tank.

Corroboration of Analytical Results

Measurement of ^{238}U Short Lived Daughters

In addition to using the ^{235}U peaks from the gamma ray spectroscopy measurements, the ^{234}Th peaks were measured. As shown in Figure 2.1, ^{234}Th is a decay product of ^{238}U and emits two gamma rays, one at 63 keV and one at 93 keV which are labeled in Figure 5.1. Table 5.3 shows the estimated activity of each tank with respect to uranium and the estimated thorium activity based on the peak area of the 93 keV gamma-ray. Protactinium-234m directly results from the decay of ^{234}Th and emits a 1001 keV gamma ray (0.6%) that was used to obtain $^{234\text{m}}\text{Pa}$ activity.

As seen from the comparison in activities, both ^{234}Th and $^{234\text{m}}\text{Pa}$ are present in the hot water tanks. The activities are based on the absolute detector efficiency of 0.041% (^{234}Th) and 0.0099% ($^{234\text{m}}\text{Pa}$) determined using the ^{152}Eu absolute detection efficiency curve scaled to the hot water tank geometry (Appendix C).

Table 5.3 Hot Water Tank Activity, Specifically ^{238}U , ^{234}Th , and $^{234\text{m}}\text{Pa}$

Location Identification number	Activity (MBq) From			
	Total Uranium	^{238}U	^{234}Th	$^{234\text{m}}\text{Pa}$
1	0.14	0.069	0.038	0.18
2 a	0.31	0.15	0.060	0.48
2 b	1.7	0.83	0.47	2.1
3	0.10	0.050	0.020	0.055
4	0.73	0.35	0.22	1.00

The activities of these two radionuclides are quite different from each other, with the ^{238}U activity approximately twice that of the thorium and typically less than the protactinium. Measurements for the amount of thorium and protactinium were not taken for the water entering or exiting the hot water tanks, nor were the solubilities and kinetics of the reactions for these components explored. It is also possible that the thorium is less likely to precipitate (once formed) or readily dissolves back into the water while the uranium and $^{234\text{m}}\text{Pa}$ continues to accumulate. Regardless, the presence of these decay products of uranium corroborates the presence of ^{238}U . Additionally, this activity is also another form of TENORM that should be considered in the overall effect of radionuclides inside the hot water tank.

Gamma-ray Imaging

To determine the spatial distribution of uranium in the tank, gamma-ray imaging was performed on hot water tank 4. Figure 5.2 is a graphical representation of the data obtained from these measurements. Absolute activities were not obtained because of the unknown detector efficiency for this geometry. However, each measurement was taken

under the same conditions, therefore the net count rate (cpm) in each region for the 186 keV gamma-ray peak areas can be compared. The figure is composed of five pie charts, representing the five levels where readings were taken (high, mid high, middle, mid low, and low), and correspond to the location at the tank. Additionally, there are four pieces in each pie; representing the four locations at each level where readings were taken. The figure is oriented such that the "12 o'clock" position is on top.

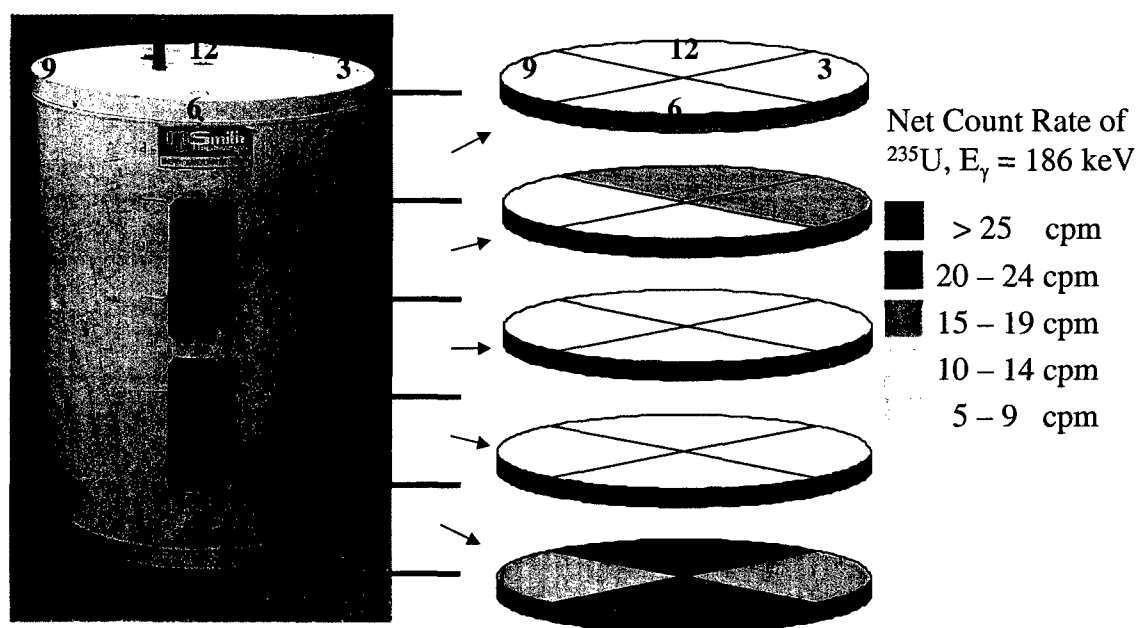


Figure 5.2 Graphical Representation of Uranium Precipitation Location Inside Hot Water Tank

It appears the uranium accumulates toward the bottom of the tank, which is expected if the uranium is precipitating. The imaging was performed with the heating

elements in place, which is consistent with the locations of the highest count rates observed. This helps explain why the 6 and 12 o'clock positions on the low level, where the heating element is located, have higher count rates than the 3 and 9 o'clock positions. Generally, at higher levels in the tank, the count rates decrease. However, this doesn't hold true at the mid high level, one level from the top. One explanation for this is the presence of another heating element which is located right between the middle and mid high levels.

Sediment spilled out of the tank prior to the gamma-ray imaging taking place. The tank was stored outside, and rainwater entered the tank. When the tank was being moved, the water and some sediment was drained out of the plug located at the 6 o'clock position on the bottom level. This sediment was recovered, and was used for the XRF analysis. This loss of sediment may have resulted in the count rates at the low position being lower than would have otherwise been recorded, but was not quantified.

X-Ray Fluoroscopy

Sediment from hot water tank 4, scale from both of the heating elements of tank 4, and scale from the heating element from tank 1 were analyzed by XRF to corroborate the presence of uranium and to identify other precipitated elements. The masses of each of these samples were different. Also, the solid samples were not pressed or fused into a standard geometry and the sample matrix was not matched to standards; therefore only qualitative determinations of the elements present can be made. The relative intensities of the elements cannot be compared within a given sample because of differences that likely exist in their calibration curves, but the relative intensity of a given element from different samples is comparable. Table 5.4 contains the results from the XRF analysis

Table 5.4 XRF Qualitative Analysis Results for Intensities of Elements Present Relative to Uranium (Intensity U/ Intensity Component)

Component	O	Na	Mg	Si	P	S	Cl	K	Ca	Mn	Fe	Cu	Zn	Sr	Pb	U
Sample																
Tank 1 Heating Element Scale	325	1009	ND	168	11.5	317	195	73.6	35.9	418	0.97	41.9	8.85	ND	ND	1
Tank 4 Sediment	82.6	ND	30.4	6.1	4.2	6.6	169	6.9	0.35	222	5.55	11.9	27.9	13.7	49.3	1
Tank 4 Bottom Heating Element Scale	254	ND	850	191	15.3	77.2	ND	ND	4.21	ND	54.6	60.7	ND	ND	216	1
Tank 4 Top Heating Element Scale	131	480	628	200	6.5	34.9	ND	ND	1.7	1813	40	14.4	ND	ND	ND	1

relative to the uranium intensity. Additionally the raw intensity (kcps) for the background sample, and sample raw intensity datum are located in Appendix D.

The elemental ratios provided in Table 5.4 provide the ability to compare among the samples the various elements identified relative to uranium. As seen, uranium is present in all of the samples (and at a relatively high intensity from Appendix D) consistent with the gamma ray spectroscopy measurements. There are a few similarities between the tanks worth noting. First, the scale from all three of the heating elements appears to contain relatively little silicon as compared to calcium and uranium, as expected due to scaling. Additionally, the sediment from tank 4 contains a relatively high intensity of silicon and calcium as compared to uranium, which corresponds to the sandy composition of the sample. The two heating elements from tank 4 have a relative intensity for uranium/calcium that are of the same order of magnitude, which differs from the sediment from that tank by an order of magnitude. If the uranium actually precipitates as a mineral, this tends to suggest it is precipitating as a calcium-uranium species mineral over a silicon-uranium species mineral, since the uranium/calcium ratio is closer to 1. However, as will be shown in the geochemical modeling section both calcium and silica precipitates without the uranium, as occurs in routine scaling.

Geochemical Computer Modeling

Precipitation

Modeling of the hot water tank as an individual environment using the well water parameters in Table 4.1 was performed using both the MINTEQA2 and Geochemist's Work Bench. Both models were run using the average parameter value, as well as the maximum and minimum values. No appreciable differences in the predictions from the

two models were noticed in this range of input values. The models were run varying the pH as well as the temperature. Eh was also varied with no noticeable effects on the precipitation. The variation of pH had an impact on the composition of the aqueous phase uranium as well as the composition of the precipitate predicted by the models. Similarly, the temperature variation was significant in these predictions. Figure 5.3 and 5.4 are graphical speciation diagrams as predicted by The Geochemist's Work Bench. In both graphs, species in italics represent aqueous phases, while other species are solids. It is predicted that the uranium is in the form of $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ when it enters the hot water tank at ground water temperature (20°C).

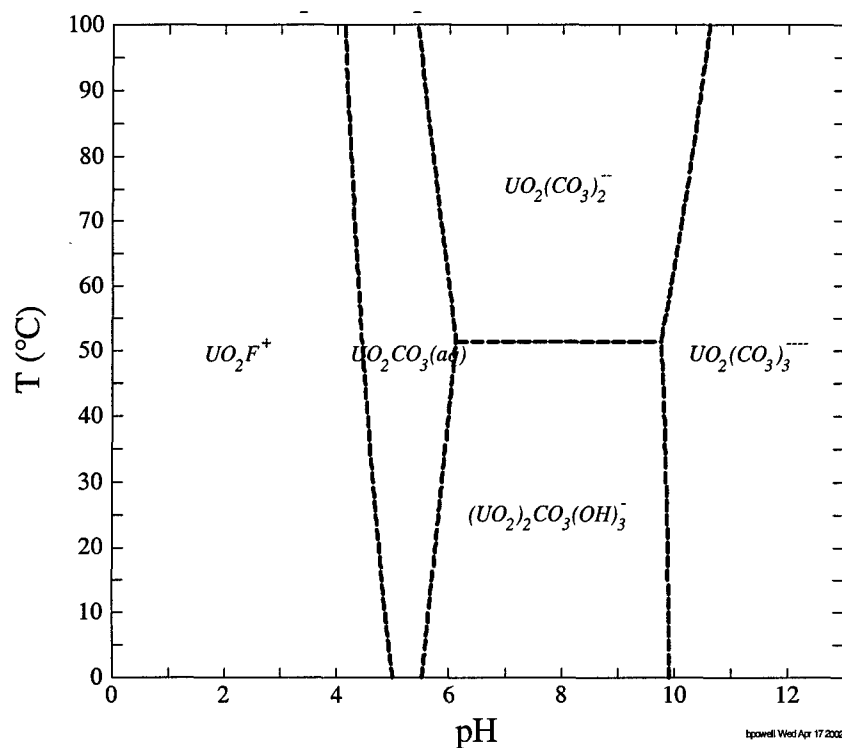


Figure 5.3 The Geochemist's Work Bench Aqueous Speciation Prediction Using Input Parameters From Simpsonville Well Water (UO_2^{+2} concentration = 0.8 mg/L).

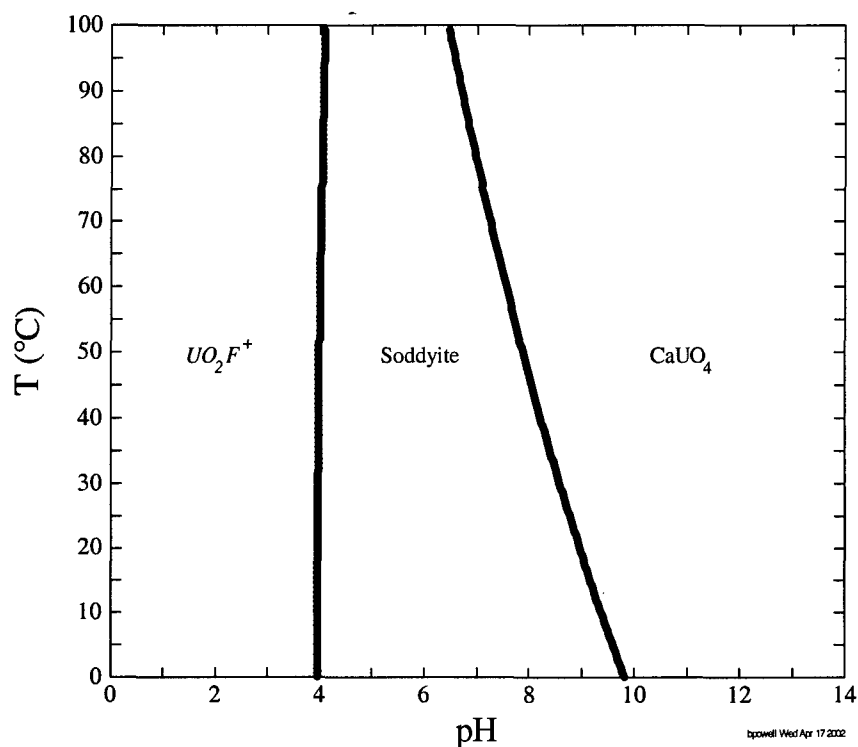


Figure 5.4 The Geochemist's Work Bench Precipitation Speciation Prediction Using Input Parameters From Simpsonville Well Water

Both models predicted that independent of temperature, the dissolved uranium would precipitate, either as a calcium based mineral, $CaUO_4$ (database $K_{sp} = 1.1 \times 10^{16}$) at high temperatures, or as a silica based mineral, Soddyite (database $K_{sp} = 3.25$), $(UO_2)_2(SiO_4) \cdot 2(H_2O)$ at lower temperatures, for pH greater than 4. It is suspected that the water coming into the system is not in thermodynamic equilibrium. The reason for this is based on the water quality parameter concentrations, which results in the computer models predicting precipitation of solids even at the ambient temperature of the ground water. If the system were in equilibrium, there would not be any elements supersaturated in the aqueous phase and precipitation would not occur unless conditions changed. Note that measurements of filtered and unfiltered groundwater had the same uranium

concentration, indicating that there are not suspended solids greater than 0.1 μm in the water (Ayaz et al., 2001). Assuming saturated equilibrium conditions in the ground water, the models predict a maximum uranium concentration of $9 \times 10^{-5} \mu\text{g/L}$, which is significantly lower than measured. Additionally, the model predicts the ground water is supersaturated in silica. At 20 $^{\circ}\text{C}$ the calcium uranium mineral is not predicted to precipitate until the pH exceeds 8.5. As a result, based on these modeling parameters, the probable mineral present in the ground under thermodynamic equilibrium would be Soddyite.

Given the parameters of the ground water entering the hot water tank, the Geochemist's Work Bench predicts that either Soddyite or CaUO_4 precipitates. MINTEQA2 provides a similar prediction, which is expected since both programs use a similar thermodynamic database for the modeling. MINTEQA2 predicts the possibility of an additional uranium species, Haiweeite (database $K_{\text{sp}} = 4.7 \times 10^{-7}$), $\text{Ca}(\text{UO}_2)_2\text{Si}_6\text{O}_{15} \cdot 5(\text{H}_2\text{O})$, at pH ranges of 6.9 – 7.5, in addition to the CaUO_4 . It is suspected that as the temperature increases to approximately 70 $^{\circ}\text{C}$ inside the hot water tank the kinetics of the precipitation reactions increases. In addition to the uranium containing minerals, the models predict that quartz, SiO_2 , and tremolite, $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$, form, but the mass of these minerals decreases with the presence of uranium. These modeling predictions corroborate the XRF results of the sediment in the hot water tank. Although neither quantitative nor mineral specific, the XRF results show the potential for these minerals to be present given the fact that the elements are present in the sediment. The prediction that the mineral species precipitating changes at elevated temperatures from a silica based mineral to a calcium based mineral (at the same pH)

might explain the accumulation of uranium in the hot water tank, if the kinetics of this formation are faster.

Dissolution

Both models predicted that uranium solids present in the hot water tank would dissolve once clean water entered into the system. The models were run using an infinite solid of the minerals predicted above (each mineral was run separately, CaUO_4 , Soddyite, and Haiweeite). With all of the runs, the model predicts that the uranium dissolves into the post-treatment water. The modeling also predicts that some of the dissolved uranium precipitates as one of the minerals mentioned above, depending on pH. For example, if Soddyite is put in as the infinite solid, then once it dissolves it is now present in the aqueous phase. Given thermodynamic equilibrium a solid species precipitates depending on the pH assigned to the model (namely, CaUO_4 , Soddyite, and Haiweeite). The dissolved equilibrium concentration of uranium ranges from $0.05 \mu\text{g/L}$ to $1.2 \times 10^{-4} \mu\text{g/L}$, depending on the mineral that is the infinite solid and the pH. The highest dissolved concentration is predicted when CaUO_4 is the mineral and the system is at a pH of 5.9. At a pH range of 7 – 8, the dissolved concentration was predicted to be around $2 \times 10^{-3} \mu\text{g/L}$, regardless of the uranium mineral present as the infinite solid.

Modeling Synopsis

With both modeling scenarios (precipitation and dissolution) there is confirmation of uranium being present in the phases expected. Actual conditions are quite likely to be different from the equilibrium conditions present in the model, potentially explaining the difference in model predictions and field measurements and prohibiting an exact determination as to speciation of uranium inside the hot water tanks. The primary reason

the exact speciation cannot be determined is because kinetics and sorption processes are not incorporated into the modeling programs.

Chapter 6

SUMMARY AND CONCLUSIONS

The objective of this research was to determine if uranium in ground water could concentrate inside the hot water tanks of homes in the Simpsonville community resulting in the hot water tank being classified as TENORM. Uranium concentrations in the private wells of many of the residences in the Simpsonville area exceed the MCL set by the EPA, with some of them being 100 times greater. In some cases, corrective actions have already been accomplished, by either in-house treatment or connection to a municipal water supply. But numerous other homes are outside the economical reach of the municipal water supply. These corrective actions elevate uranium entering the house, but does not in and of itself remove the presence of uranium in the home. Uranium has been shown to precipitate and accumulate in the hot water tanks of these homes, resulting in a reservoir available for further distribution. Although not a direct radiation dose exposure hazard due to its presence in the tank, uranium remains in the hot water system of the home. Gamma-ray spectroscopy has shown that uranium concentrates in the hot water tank. XRF analyses confirms the presence of uranium along with other elements, most notably calcium and silicon. Additionally, post treatment hot water drinking water samples show that the uranium will dissolve back into the clean water, sometimes creating a situation where the water now exceeds the EPA MCL of 30 $\mu\text{g/L}$. Both the precipitation and dissolution of uranium in the hot water tanks were predicted with thermodynamic equilibrium models.

APPENDICES

Appendix A

Kinetic Phosphorescence Analyzer

KPA Start Up

The KPA system start-up is done by turning on all four switches (CPU, monitor, printer, and KPA). Secondly, use the arrow to go down to "KPA" and press enter. Next, at C: KPA/, type KPA and press enter. Then load the calibration you wish to use. (Press F2, Calibrate. Press F4, Load Calibration. Place cursor over the calibration you wish to use. Press enter to load the calibration. Wait while the computer loads the calibration. Check the bottom right hand corner of the screen for the calibration equation to make sure it is the one you intended to load.) Once the calibration is loaded, press Esc to return to the Calibration Menu. Press Esc to return to the Main Menu, and then press F1 to get to the Analysis Menu. Finally, press F1 to analyze a sample.

Sample Preparation

Sample preparation encompasses multiple steps and begins by cleaning the cuvettes. First, using tweezers remove the cap and place it upside down on the counter. Secondly, vacuum out all of the old cuvette contents. Next, half-fill the cuvette with 1M H_2SO_4 , replace the cap and invert several times. Remove the cap again with tweezers, place on counter, and vacuum out the acid solution. Then, fill the cuvette with DDI water above the rim and vacuum out. Repeat the water wash step two to three times. Once complete, half-fill the cuvette with URAPLEX and tip to ensure contact with all of the sides, and then vacuum out URAPLEX. Rinse cap with DDI water and dry using Kimwipe. Prepare a 1 mL sample for quantification by adding 1.5 mL of URAPLEX. It

may be necessary to dilute the sample to prevent quenching or saturation when using natural water sources.

Results Analysis

Many factors reported in the analysis can help determine if the KPA results are precise, or if the sample needs to be altered before analysis. The following parameters should be checked on every sample to determine the quality of the result: 1) The lifetime should be between 200 and 300 μs . If the lifetime is out of this range there may be a quenching problem and the sample may need to be diluted. Deviations up to 150 – 350 μs can be acceptable, but is based on experience and knowledge of the sample. 2) The reference ratio should be above 0.85. If the reference ratio is lower than this, then the reference solution should be replaced and the system recalibrated. 3) The R^2 value should be ≥ 0.995 . If lower than this then try measuring in the other range setting. If this still doesn't work, then the sample is either too low in uranium concentration or it is contaminated. 4) The reported intensity should have the notation ($t = 52 \mu\text{s}$) beside it. If this parameter is any value beside 52 μs it indicates gate shifting or gate dropping. Try to correct by using the other calibration range. If the intensity is still out of spec then the sample probably needs to be diluted.

Appendix B

Alpha Spectroscopy For Location 2 Water

The following spectra are from water samples collected at location 2. The program/equipment used for the analysis was not Y2K compliant, and as a result, the date shown on the spectra are the year 1901, when in reality it was 2001.

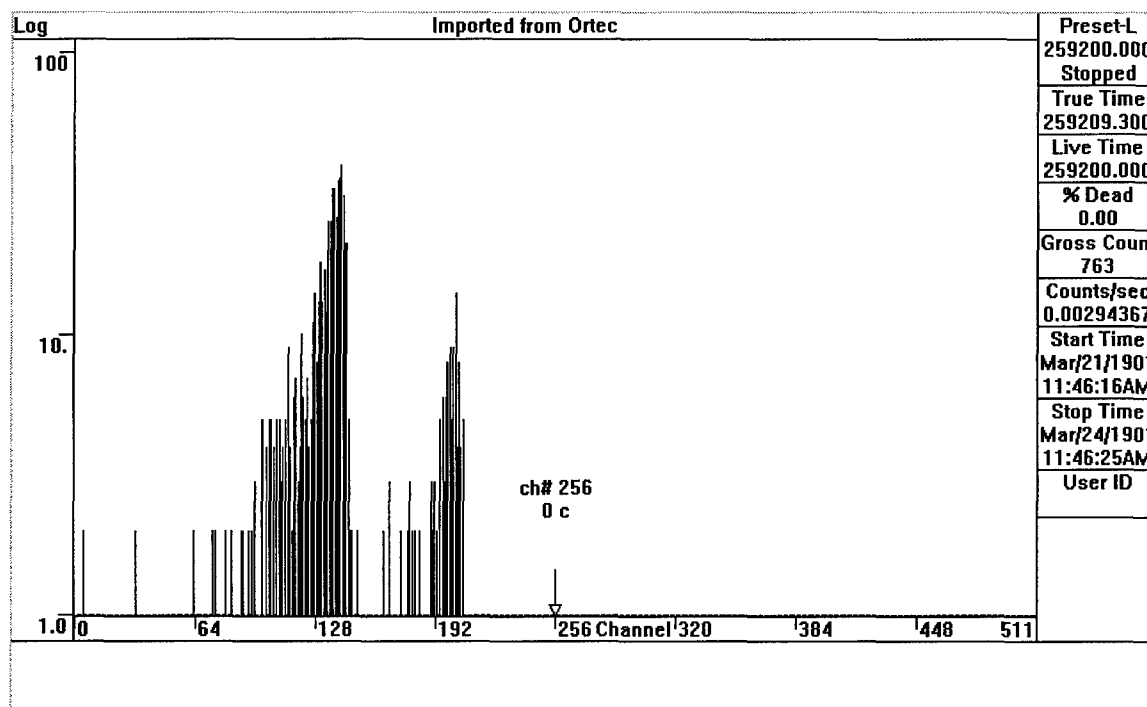


Figure B.1 1000 $\mu\text{g/L}$ 10ml U Standard

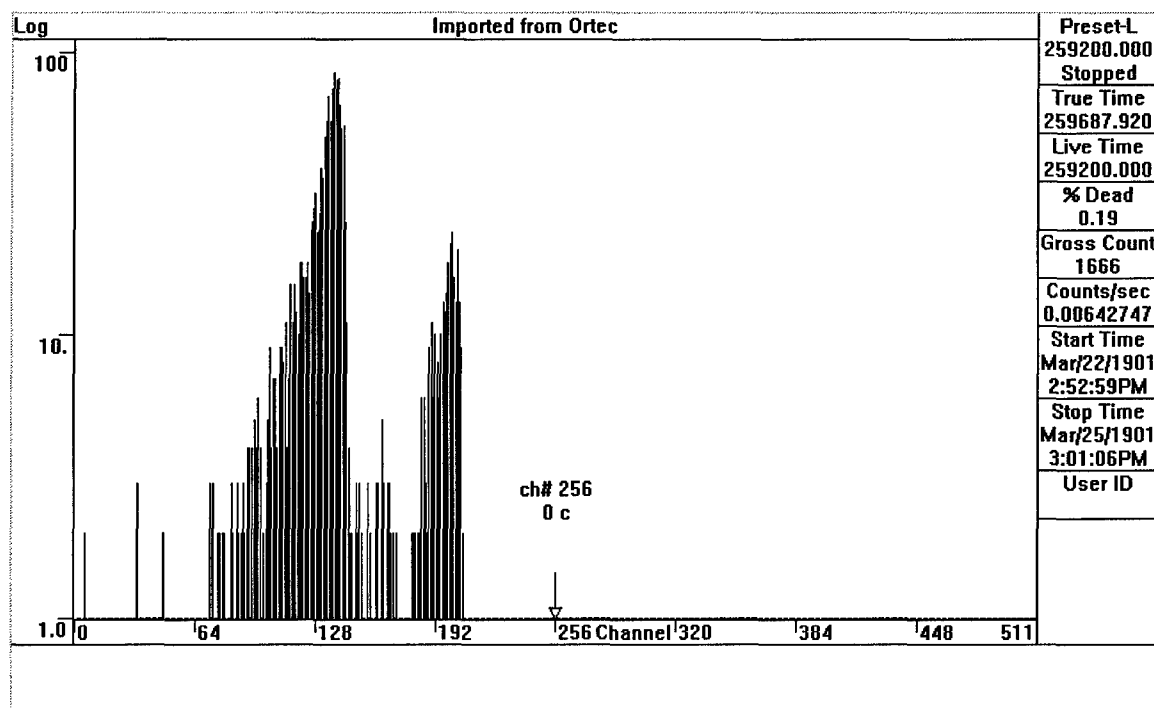


Figure B.2 2000 $\mu\text{g/L}$ 10ml U Standard

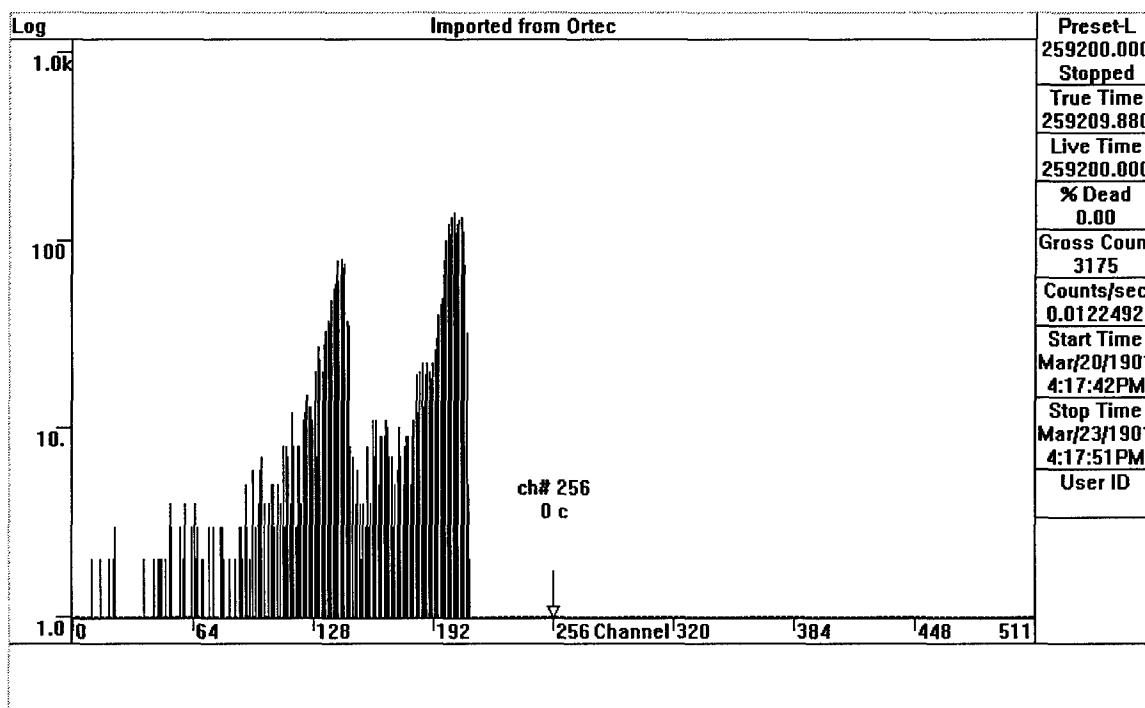


Figure B.3 Location 2 Cold Water 10 ml Sample

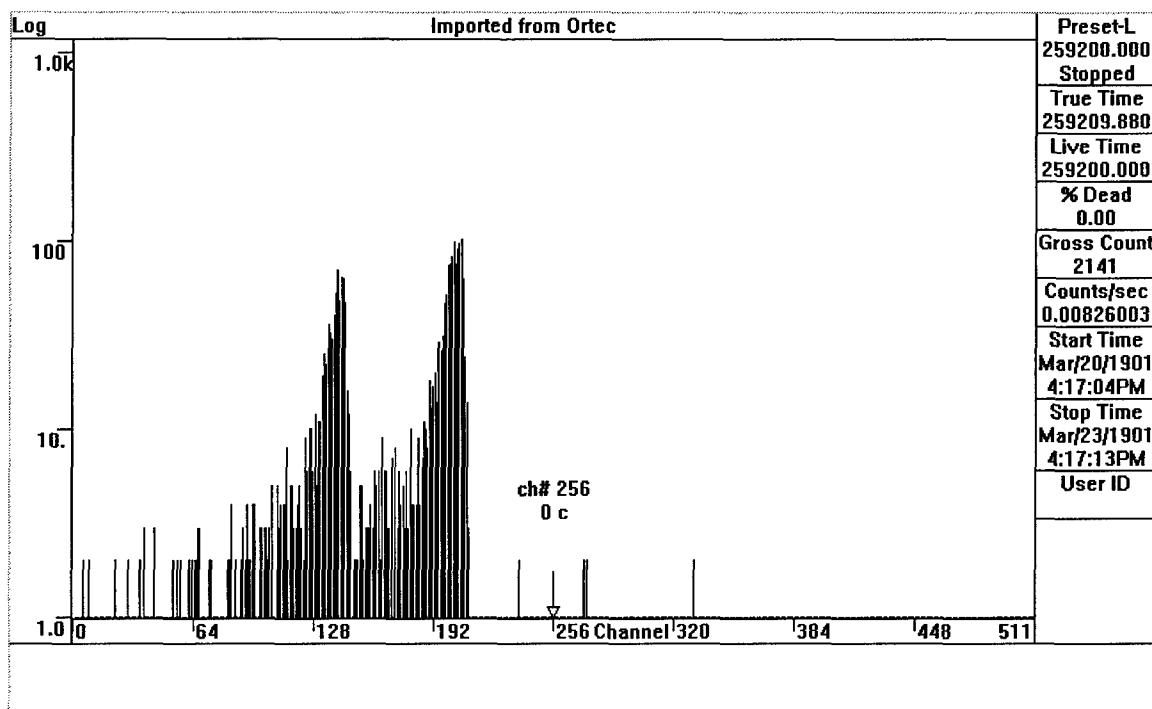


Figure B.4 Location 2 Hot Water 10 ml Sample

Appendix C

Energy and Efficiency Calibration

The HPGe was energy and efficiency calibrated using the following sources: ^{60}Co (5.26yr half life, 1.173, 1.332 MeV gamma-ray energy peaks, 1 μCi on 4/96 produced by Oxford), ^{137}Cs (30.2yr half life, 0.662 MeV gamma-ray energy peak, 1 μCi on 4/96 produced by Oxford), and ^{152}Eu (13.6yr half life, 0.0401, 0.0454, 0.1218, 0.2447, 0.3443, 0.4111, 0.4439, 0.7789, 0.8673, 0.964, 1.0858, 1.0897, 1.112, and 1.408 MeV gamma-ray energy peaks, 1.080 μCi on June 1, 1993, produced by Isotope Products Laboratories, number 433-23). ^{60}Co and ^{137}Cs sources were used first and placed 4 inches (measured from the end of the detector to the center of the source) from the detector. A spectrum was collected for 90 seconds. Then, ^{152}Eu was used in the same geometry setup and produced the data in Table C.1. An efficiency calibration for ^{152}Eu was also accomplished at 30cm from the detector (measured from the tip of the detector to the center of the source). Using the calibration data, an efficiency calibration curve was developed for the detector. That curve is shown in Figure C.1.

Table C.1 ^{152}Eu Energy Calibration Data

Source	Energy of photon (keV)	Channel #	Emission Fraction	Area of ROI (Counts)	Efficiency from Data	Fit Efficiency
^{152}Eu	40.1	162	0.58554	968	0.000691	0.000797
	45.4	185	0.1464	309	0.000882	0.000749
	121.7	493	0.28432	948	0.001394	0.001476
	244.69	990	0.074935	253	0.001411	0.001157
	344.27	1393	0.26488	429	0.000677	0.000867
	411.11	1663	0.022144	30	0.000566	0.000736
	443.98	1796	0.031135	57	0.000765	0.000685
	778.89	3151	0.12741	139	0.000456	0.000403
	867.32	3508	0.041601	23	0.000231	0.000364
	964.01	3900	0.14441	113	0.000327	0.00033
	1085.8	4393	0.09963	74	0.00031	0.000295
	1112	4499	0.13302	76	0.000239	0.000288
	1408	5698	0.20747	151	0.000304	0.000231

The best fit line was then calculated using the following efficiency (ϵ) equation:

$$\epsilon = a_1 E_\gamma^{-a_2} + a_3 e^{(-E_\gamma a_4)} \quad (6)$$

Running Microsoft Excel solver and minimizing the sum of the efficiency from the data minus the fit efficiency quantity squared the following variable values were obtained:

$$a_1 = 0.217$$

$$a_2 = 0.944$$

$$a_3 = -0.015$$

$$a_4 = 0.024$$

From this, the efficiency calibration curve for the HPGe was developed and is provided in Figure C.1.

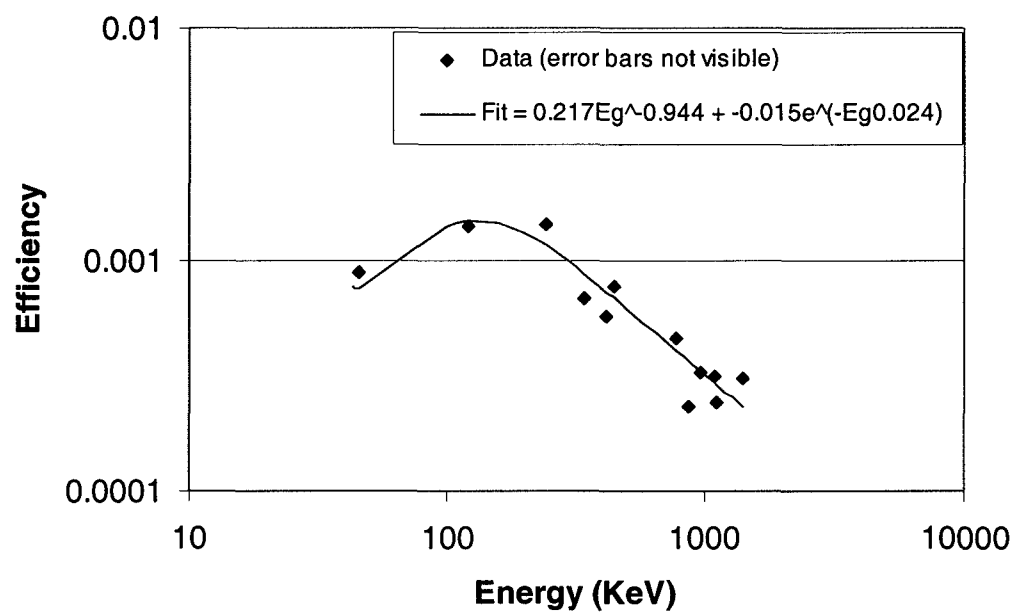


Figure C.1 Efficiency Calibration Curve With Source 30 cm From Detector

Appendix D

XRF Data

Table D.1 XRF Qualitative Analysis Results for Intensities of Elements Present (Intensities in kcps)

Component	O	Na	Mg	Si	P	S	Cl	K	Ca	Mn	Fe	Cu	Zn	Sr	Pb	U
Sample																
Tank 1 Heating Element Scale	0.179	0.057	ND	0.347	5.05	0.184	0.299	0.79	1.62	0.139	60.1	1.39	6.57	ND	ND	58.22
Tank 4 Sediment	0.204	ND	0.553	2.75	3.96	2.56	0.099	2.43	47.5	0.076	3.03	1.41	0.60	1.22	0.34	16.82
Tank 4 Bottom Heating Element Scale	0.258	ND	0.077	0.344	4.30	0.85	ND	ND	15.6	ND	1.19	1.09	ND	ND	0.30	65.6
Tank 4 Top Heating Element Scale	0.209	0.057	0.043	0.136	4.21	0.78	ND	ND	15.7	0.015	0.67	1.88	ND	ND	ND	27.2
Background	0.13	ND	ND	0.06	3.92	ND	ND	ND	0.099	ND	ND	ND	ND	ND	ND	ND

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